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A Mechanism for the Decomposition of Ethylene Oxide

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The thermal decomposition of ethylene oxide exhibits an induction period, and is inhibited by the addition of inert gases. The assumptions that ethylene oxide mainly isomerizes to acetaldehyde, but at the same time produces free radicals which induce a chain decomposition of the acetaldehyde, and that the recombination of methyl radicals requires a third body lead to expressions for the length of the induction period and the pressure change during a run in qualitative agreement with experiments by Heckert and Mack.

THE thermal decomposition of ethylene oxide, studied by Heckert and Mack,[1] has a number of unusual features. The decomposition is homogeneous in Pyrex, and follows the equation

$$(CH_2)_2O = CH_4 + CO.$$

There is a pronounced "induction period," lasting about thirty minutes at 380°C, which decreases as the temperature is increased; the pressure-time curve is therefore S shaped. After the induction period is over the reaction is approximately first order. The addition of inert gases increases the induction period considerably, and decreases the rate of the reaction as a whole. The mechanism proposed by Heckert and Mack, the production of an excited acetaldehyde molecule, which then decomposes to CH_4+CO or is deactivated by collision, has been shown to be improbable by Kassel.[2]

Consideration of the structure of ethylene oxide indicates that the initial step of Heckert and Mack's mechanism, the conversion of ethylene oxide to acetaldehyde, is quite plausible, especially since an analogous reaction, the conversion of cyclopropane to propene, is known.[3] It is also known that if free radicals are introduced into acetaldehyde a chain decomposition of the acetaldehyde is set up,[4] which proceeds rapidly at a temperature considerably lower than that at which acetaldehyde will react alone. The isomerization of ethylene oxide to acetaldehyde accompanied by the production of a few free radicals would, therefore, lead to the observed reaction. It is the purpose of this paper to show that a mechanism of this sort will account for many of the features of the decomposition of ethylene oxide.

If we suppose, then, that ethylene oxide usually reacts by forming acetaldehyde, but that occasionally a free radical is formed which reacts with acetaldehyde just as methyls do, we can set up the following sequence of reactions:[5]

[1] Heckert and Mack, J. Am. Chem. Soc. **51**, 2706 (1929).
[2] Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Co., 1932), p. 284.
[3] Chambers and Kistiakowsky, J. Am. Chem. Soc. **56**, 399 (1934).
[4] Allen and Sickman, J. Am. Chem. Soc. **56**, 2031 (1934).
[5] All free radicals are denoted by R, and are assumed to react in the same way; the main chain carrier presumably is, however, the methyl radical produced by II. The chain breaking step IV is assumed to require a third body M, whose effect is absorbed in the rate constant k_4.

$$\text{I.}\quad \underset{\text{O}}{\text{CH}_2\text{—CH}_2} \rightarrow 2\text{R} \qquad k_1$$

$$\text{II.}\quad \underset{\text{O}}{\text{CH}_2\text{—CH}_2} \rightarrow \text{CH}_3\text{CHO} \qquad k_1'$$

$$\text{III.}\quad \text{R}+\text{CH}_3\text{CHO}\rightarrow\text{RH}+\text{CH}_3\text{CO}\rightarrow\text{RH}+\text{CO}+\text{R} \qquad k_2$$

$$\text{IV.}\quad 2\text{R}+\text{M} \rightarrow \text{X}+\text{M} \qquad k_4$$

Concentration of	$(CH_2)_2O$	R	CH_3CHO
Given by	c_1	c_2	y

Following Rice and Herzfeld,[6] a steady state equation for the concentration of free radicals may be set up,

$$dc_2/dt=2k_1c_1-2k_4c_2^2=0, \tag{1}$$

or

$$c_2=(k_1c_1/k_4)^{\frac{1}{2}}. \tag{2}$$

The rate at which ethylene oxide disappears is given by

$$-dc_1/dt=k_1c_1+k_1'c_1=\kappa c_1, \tag{3}$$

where

$$\kappa=k_1+k_1'\backsimeq k_1' \quad \text{if} \quad k_1\ll k_1'. \tag{4}$$

The concentration of ethylene oxide at any time t is given by integrating (3), which gives, if A is the initial concentration of ethylene oxide,

$$c_1=A\ \exp\ (-\kappa t). \tag{5}$$

Now acetaldehyde is being formed and decomposed at the same time by reactions II and III; its net rate of formation is given by

$$\begin{aligned} dy/dt&=k_1'c_1-k_2c_2y=k_1'c_1-k_2(k_1c_1/k_4)^{\frac{1}{2}}y \\ &=k_1'A\ \exp\ (-\kappa t)-k_2(k_1A/k_4)^{\frac{1}{2}} \\ &\qquad\times\exp\ (-\kappa t/2)y, \end{aligned} \tag{6}$$

by substituting for c_1 from (5).

It is now convenient to set $\exp\ (-\kappa t/2)=x$, which maps the t axis from zero to infinity on the x axis from one to zero. Eq. (6) becomes

$$\begin{aligned} dy/dx&=-2k_1'Ax/\kappa+2k_2y(k_1A/k_4)^{\frac{1}{2}}/\kappa \\ &=-Qx+Py, \end{aligned} \tag{7}$$

where

$$P=2k_2(k_1A/k_4)^{\frac{1}{2}}/\kappa \quad \text{and} \quad Q=2k_1'A/\kappa\backsimeq 2A. \tag{8}$$

The integral of this equation, giving the concentration of aldehyde at any time, or rather x value, during a run, remembering that at $t=0$, $x=1$ and $y=0$, is

$$y=Q/P^2\{1+Px-(1+P)\ \exp\ [-P(1-x)]\}. \tag{9}$$

The concentration of aldehyde given by this equation has a maximum during a run given by setting $dy/dx=0$. The x value at which y reaches this maximum is

$$x^*=1-(1/P)\ \log\ (1+P). \tag{10}$$

Finally, the total pressure p during the run is given by

$$\begin{aligned} p&=c_1+y+2(A-c_1-y)=2A-c_1-y \\ &=2A-Ax^2-2A/P^2\{1+Px \\ &\qquad-(1+P)\ \exp\ [-P(1-x)]\}. \end{aligned} \tag{11}$$

This expression is easily seen to have the form given by the experimental data, and the latter may be used to get an idea of the magnitude of the constant P.

The value of x^* is that given by the inflection point in the pressure-time curve for the reaction.[7] For Heckert and Mack's[1] run 168m ($A=107.42$ cm) this is about 30 minutes, and with their k_1 as κ, $P\backsimeq 190$.

Furthermore, P should have a positive temperature coefficient, so that raising the temperature will increase P. From (10) we see that increasing P increases x^*, and thus shortens the induction period, as is found experimentally.

Inert Cases

So far we have neglected the assumption that reaction IV requires a third body and that k_4 depends on the concentration of everything present in the reaction vessel, which precludes the possibility that (11) will hold exactly. According to the scheme presented,[8] the only effect of

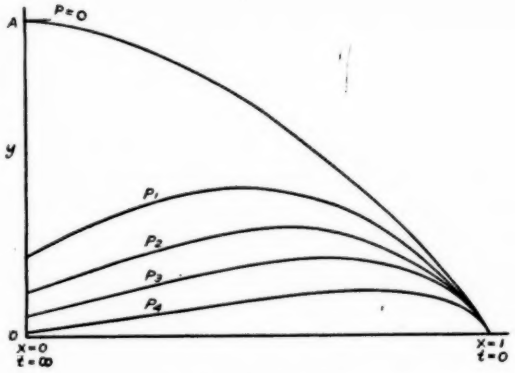
[6] F. O. Rice and Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).

[7] This is not exactly true, as x^* as defined here is the inflection point of the p, x curve, which is not identical with that of the p, t curve. Strictly, P should be calculated from the equation $1-x'=(1/P)\ \log\ (1+P+Px'+P^2x')/(2Px'+1)$ obtained by setting $d^2p/dt^2=0$, where x' is the x value of the inflection point on the p, t curve. Since $P\gg 1$,

$$x'\backsimeq 1-(1/P)\ \log\ (P/2)\backsimeq x^*+(1/P)\ \log\ 2,$$

and P becomes 160 instead of 190 as above.

[8] I and II are assumed unimolecular and first order. If they have "fallen off" to any considerable extent the effect of adding inert gases will be decreased, as I and II will then be increased simultaneously with IV. The further modifications necessary in this case are easily made. Experimentally, P decreases with increasing A but κ remains almost constant, so that apparently k_1 has fallen off considerably.



$0<P_1<P_2<P_3<P_4$

FIG. 1. Schematic diagram of the concentration of aldehyde y as a function of the "time function" $x=\exp(-\kappa t/2)$.

adding inert gas will be to increase k_4, and therefore to decrease P. That decreasing P increases the induction period has already been pointed out; the general effect of changing P may be seen from the following.

Consider dy/dx for two values of P, P_1 and P_2, where $P_1>P_2$, all other quantities being the same, and let the corresponding values of y be y_1 and y_2. Then

$$dy_1/dx-P_1y_1=-Qx, \qquad \text{(a)}$$

$$dy_2/dx-P_2y_2=-Qx. \qquad \text{(b)}$$

Subtracting (b) from (a) and adding P_1y_2 to each side we get

$$d(y_1-y_2)/dx-P_1(y_1-y_2)=(P_1-P_2)y_2.$$

Now set $z=y_1-y_2$, and multiply each side by $\exp(-P_1x)$. Then

$$(dz/dx-P_1z)\exp(-P_1x) = (P_1-P_2)y_2\exp(-P_1x). \qquad \text{(c)}$$

The left-hand side of (c) is equal to $d[z\exp(-P_1x)]/dx$ and the right-hand side is positive for $0<x<1$. The function $z\exp(-P_1x)$ is therefore a monatonic increasing function of x. Now when $x=1$, $y_1=y_2=0$, and therefore $z=z\exp(-P_1x)=0$, so that for all $x<1$, $z\exp(-P_1x)$ is negative, and since $\exp(-P_1x)$ is always positive, $z=y_1-y_2<0$, or $y_2>y_1$. Thus if P is decreased y is increased at all times during the run. Fig. 1 is a schematic diagram of y as a function of x for different values of P. An increase of y means a corresponding decrease in the observed pressure, and adding inert gas should therefore decrease the rate of the reaction, again in agreement with experiment.

THE INITIAL REACTION

If, as seems reasonable, we can identity κ with k_1', we can draw some conclusions as to the mechanism of reactions I and II. Heckert and Mack[2] find $k_1'=10^{13}\exp(-5200/RT)$ sec.$^{-1}$. This is definitely in favor of a bond breaking mechanism[9] such as

$$\begin{array}{c}CH_2-CH_2\\ \diagdown\ \ \diagup\\ \ \ O\end{array} \xrightarrow{k_1} -CH_2-CH_2-O- \xrightarrow{k_1'} CH_3CHO;$$

the "2R" of I would then be $-CH_2-CH_2-O-$. This mechanism assumes that the ring opens only at the C–O bond. An equally plausible mechanism would be to assume that the $-CH_2-CH_2-O-$ radical rearranges at once to acetaldehyde, but that occasionally the ring opens at the C–C bond, giving $-CH_2-O-CH_2-$. This radical might then react as the "2R" of I, or it might split off CH_2O, forming a CH_2. In any case the mathematical equations would be unchanged.

THE RECOMBINATION OF METHYL RADICALS

F. O. Rice and Herzfeld[6] assume that methyls recombine by a bimolecular association, while the mechanism assumed here requires a three-body reaction, which also seems preferable theoretically. It should be pointed out, however, that the chain decomposition of acetaldehyde induced by azomethane[4] seems to be consistent with a bimolecular association. The implications of IV requiring a third body in other reactions will be discussed elsewhere.

[9] O. K. Rice and Gershinowitz, J. Chem. Phys. **3**, 485 (1935).

Wave-Mechanical Treatment of the LiH Molecule

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Variational treatments of the LiH molecule and LiH^+ ion have been carried out in which the two electrons of the inner shell of the Li atom are represented by Slater wave functions and the orbitals of the two valence electrons are treated after the method of James and Coolidge (but without the interelectronic distance as one of the coordinates). In this treatment elliptical coordinates are used for the expression of the wave function for the outer electrons, which takes the form of an exponential times a power series. The energy matrix for the LiH molecule contain the matrix terms for the LiH^+ ion, for which calculations were also made. The lowest state of the LiH^+ ion is a $^2\Sigma$ state with the dissociation products normal hydrogen and ionized lithium and is the only one-quantum state. The use of a very flexible eleven-term function gives at an internuclear distance of three Bohr radii an energy of repulsion of 0.181 ev. The slope of the potential energy curve at this point is found to be -0.791 ev per Bohr radius. The lowest state of the ion is surely stable with an equilibrium distance somewhat greater than three Bohr radii. The energies of the four two-quantum $^2\Sigma$ states of LiH^+ at the same internuclear distance are obtained from the next four roots of the eleventh-order determinantal equation used to obtain the energy of the lowest state. These states are found to be quite strongly repulsive at this distance. On applying the variational method to the ground state of the neutral LiH molecule, it is found that the best value for the calculated binding energy that can be expected is smaller than the observed value by over a half volt. The addition of two terms containing the cosine of the difference of the azimuthal angles of the two outer electrons improves the calculated energy by 0.13 ev. An eight-term wave function has been tried for the $^3\Sigma$ state of LiH dissociating to the same products as the ground state. The energy found is a repulsion of 1.89 ev at a distance of three Bohr radii, the equilibrium distance of the ground state.

IN this paper[1] we wish to present variational treatments of the LiH molecule and LiH^+ ion based on the method of James and Coolidge. This method, first applied[2] to the ground state of H_2, is the most accurate method known for the treatment of simple molecules. For the three states of the H_2 molecule to which it has been applied, the binding energies obtained are in very satisfactory agreement with the experimental values. Hutchisson and Muskat[3] have treated the LiH molecule by wave mechanics using the Heitler-London method of atomic wave functions and a simplified Hamiltonian, obtaining results in fairly good agreement with experiment. However, James[4] has shown that the approximations made in such a treatment have very little justification and that the Heitler-London method, when applied in rigorous form, gives binding energies which are much too small.

The James-Coolidge method is characterized by (1) the use of an extremely flexible wave function involving a power series in all the coordinates and (2) the recognition of the importance of terms containing powers of the interelectronic distance. Elliptical coordinates are particularly suitable since in H_2, at least, the density function has approximately elliptical form. The terms containing the interelectronic distance make the function very sensitive to the relative positions of the electrons and serve to make it small in those parts of configuration space in which the two electrons are close together. Such terms were first introduced by Hylleraas[5] in obtaining accurate energies for the He atom. In carrying out the method a number of terms is taken and the coefficients in the series determined to make the total energy a minimum. By the variational principle, the energies obtained are upper bounds to the true energies of the system.

The LiH molecule is of particular interest because it is one of the simplest of the heteronuclear molecules. Two of its electrons are closely bound forming a closed shell about the lithium nucleus, leaving the other two as valence electrons. The

[1] A preliminary report on this work was presented at the Pittsburgh meeting of the Am. Phys. Society (Dec. 1934); see Phys. Rev. **47**, 339A (1935).

[2] James and Coolidge, Phys. Rev. **43**, 588 (1933); J. Chem. Phys. **1**, 825 (1933); J. Chem. Phys. **3**, 129 (1935). For excited states see R. Present, J. Chem. Phys. **3**, 122 (1935).

[3] Hutchisson and Muskat, Phys. Rev. **40**, 340 (1932).

[4] H. M. James, Phys. Rev. **43**, 588 (1933); J. Chem. Phys. **2**, 794 (1934). See also J. H. Van Vleck and A. Sherman, Rev. Mod. Phys. **7**, 167 (1935).

[5] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).

unobserved molecule HeH has one less electron, but all three of its electrons play the part of valence electrons. The question of inner shells has already been investigated by James[4] in his treatment of Li_2. He finds that they can be represented satisfactorily by Slater[6] one-electron functions. With such a treatment only the coordinates of the valence electrons appear in the series expression. This is a great help in simplifying the problem. However because of the mathematical complexity which still remains, it is found impracticable to include terms containing the interelectronic distance between the valence electrons. Hence, an entirely satisfactory solution is not obtained in the cases in which inner shells are present. It has been found in the treatment of H_2 and Li_2 that the method without these terms gives binding energies which are approximately one-half volt too small. Our computations on LiH give a difference of the same sign and order of magnitude. It is presumed that the difference is due to the absence of the above-mentioned terms or their equivalent, since such is the case with H_2, where no inner electrons are present.

Incidental to the solution of the problem for the neutral molecule, LiH, is the solution of the simpler problem, that of the molecular ion, LiH^+. This molecule has not been observed experimentally. A detailed treatment of it is of interest because of the accuracy of the results obtainable and because these results comprise the only information we have at the present time of its properties.

The Lithium Hydride Ion

Although, with the exception of H_2^+, we have no experimental evidence of diatomic molecules having one-electron bonds,[7] we have reason to believe from the theory that such molecules exist having stable states. That they are not observed is due to the fact that they do not have extensive discrete band spectra. The molecule H_2^+ has been shown to have at least two stable states[8] and James[9] has found that Li_2^+ has a stable ground state.

For purposes of comparison it is instructive to consider briefly the states of H_2^+, the theory of which has been worked out by Morse and Stueckelberg, Teller and others. The lowest two states are $^2\Sigma$ states and dissociate to a normal hydrogen atom and a hydrogen ion. One is symmetrical in the nuclei and stable, having a binding energy of 2.78 ev and an equilibrium distance of 2 Bohr radii, while the other is antisymmetrical and is repulsive. There are six two-quantum states (dissociating to $2s$ or $2p$ atoms and an ion) four of which are $^2\Sigma$ states. One is stable, having a binding energy of 1.35 ev and an equilibrium distance of 11·5 Bohr radii. One of the two $^2\Pi$ states is also probably stable. The behavior of the one-quantum states can be understood qualitatively as a resonance between two unperturbed atomic states with the accompaniment of a resonance energy which is subtracted in the case of the symmetrical state and added in the case of the antisymmetrical state. A similar description of the two-quantum states can be made. Here the situation is complicated by the fact that there are four interacting states. They are successively symmetrical and antisymmentrical and it so happens that only one is stable. A more careful picture might include an examination of the effect of the three-quantum states above. It is assumed that the one- and two-quantum states, which are about ten volts apart, do not affect each other appreciably.

LiH^+ is a heteronuclear molecule but its energy levels approach those of H_2^+ at infinite distances for large quantum numbers. A similar behavior can be expected at ordinary distances for those high quantum number states since in such states the valence electron is so far out that the combined field of the lithium nucleus and the shell is like that of the hydrogen nucleus. There being very little overlapping of the wave functions, the effect of interchange of valence and inner electrons is small. We would thus expect every other one of the higher $^2\Sigma$ states to take on antisymmetrical characteristics, that is to have a node near the internuclear line. Since the lithium atom has no one-quantum state, there is

[6] Slater, Phys. Rev. **36**, 59 (1930).

[7] For a recent discussion of H_2 and H_2^+ comparing experimental and theoretical results, see O. W. Richardson, Proc. Roy. Soc. **A152**, 503 (1935).

[8] Morse and Stueckelberg, Phys. Rev. **33**, 932 (1929); Teller, Zeits. f. Physik **61**, 458 (1930); Hylleraas, Zeits. f. Physik **71**, 739 (1931). See also discussion by Bethe, *Handbuch der Physik*, Vol. 24 (1933).

[9] H. M. James, J. Chem. Phys. **3**, 9 (1935).

but one one-quantum state of LiH^+ and it has the dissociation products, normal hydrogen and ionized lithium. The nearest $^2\Sigma$ state is 8.17 ev higher at infinite separation and has the dissociation products, normal lithium (Li $2s$) and ionized hydrogen. Pauling[10] has pointed out that so great a separation implies the absence of large resonance effects, such as appear in H_2^+, and he suggests that the lower state will not be stable. The four two-quantum states of LiH^+, corresponding to a dissociation into Li or H $2s$ or $2p$ and an ion, are less than 2 ev apart and hence we can expect resonance interactions and the possibility of stable states. If stable states do exist, we would expect their equilibrium distances to be large.

The lithium hydride ion is a system of three electrons and a nucleus of charge three, the lithium nucleus, separated a distance R from a nucleus of charge one, the hydrogen nucleus. Two of the electrons are closely bound forming a closed shell about the lithium nucleus. The third electron travels about one or the other or both of the nuclei as the case may be and can be thought of as a valence electron. Let distances be expressed in terms of the first Bohr radius of hydrogen and energies in a unit equal to the energy of the ground state of the hydrogen atom. The Hamiltonian of the "clamped" molecule in these atomic units is the expression

$$h=\frac{6}{R}-\sum_1^3\left(\nabla_i^2+\frac{6}{r_i}+\frac{2}{s_i}\right)+\sum_{i>j}\frac{2}{r_{ij}}, \qquad (1)$$

where ∇_i^2 is the Laplacian for electron i, r_i is its distance from the lithium nucleus and s_i is its distance from the hydrogen nucleus. The distance from electron i to electron j is r_{ij}.

We suppose that the molecular wave function can be built up as the sum of products of one-electron functions. These functions describing the behavior of single electrons we shall call orbitals. If $u(1,\alpha)$ is a valence electron orbital occupied by electron 1 with spin α, and $g(1,\alpha)$ and $g(1,\beta)$ are inner electron orbitals with spin α and β, respectively, an arbitrarily normalized wave function antisymmetrical in all the electrons is given by the determinant

$$\psi=\frac{1}{(6\int g^2dV)^{\frac{1}{2}}}\begin{vmatrix} u(1,\alpha) & g(1,\alpha) & g(1,\beta)\\ u(2,\alpha) & g(2,\alpha) & g(2,\beta)\\ u(3,\alpha) & g(3,\alpha) & g(3,\beta)\end{vmatrix}. \qquad (2)$$

For the inner electron orbitals we shall take Slater atomic wave functions. The outer electron wave function we shall express as an exponential times a power series in elliptical coordinates. All azimuthal angles will be omitted from our function. This means that not only do we restrict ourselves to the consideration of Σ states, but that we also omit a detailed treatment of the effects of the interelectronic repulsions on the wave function. By proper choice of the energy values taken for the separated atoms, some of the errors introduced in the energy of the system by these approximations will cancel out in computing the difference between the molecular energy and the total atomic energy.

Our orbitals are

$$u(1,\alpha)=\sum_f C_f f(1,\alpha),$$

$$f(1,\alpha)=\lambda_1{}^m\mu_1{}^j e^{-\delta\lambda_1}\delta(\alpha,\sigma_1), \qquad (3)$$

$$g(1,\alpha)=e^{-k r_1}\delta(\alpha,\sigma_1),\quad g(1,\beta)=e^{-k r_1}\delta(\beta,\sigma_1),$$

where $\lambda_1=(r_1+s_1)/R$, $\mu_1=(r_1-s_1)/R$ and δ and k are parameters independent of m and j. $\delta(\alpha,\sigma_1)$ is the spin function and takes the value 1 or 0 as the spin coordinate σ_1 of the electron is α or β. We can now write our wave function as a sum of determinants,

$$\psi=\sum_f C_f\psi_f,\qquad \psi_f=\frac{1}{(6\int g^2dV)^{\frac{1}{2}}}\begin{vmatrix} f(1,\alpha) & g(1,\alpha) & g(1,\beta)\\ f(2,\alpha) & g(2,\alpha) & g(2,\beta)\\ f(3,\alpha) & g(3,\alpha) & g(3,\beta)\end{vmatrix}. \qquad (4)$$

Upper bounds to the correct energies are given by minimizing the integral $I=\int\psi^* h\psi dv$ subject to the condition for normalization $1=\int\psi^*\psi dv$. The integrals are taken over all configuration space and summed over the spins. As usual in this type of problem, we obtain a secular equation for the determination of the energy values W,

$$|(F'|h|F)-W(F'|1|F)|=0,$$

where $(F'|h|F)$ and $(F'|1|F)$ are, respectively, the matrix elements of h and 1 between the functions ψ_f and $\psi_{f'}$. Methods for the evaluation of these quantities are discussed by James.[4]

[10] L. Pauling, J. Am. Chem. Soc. **53**, 3225 (1931).

Because of the large amount of numerical computation involved in obtaining the matrix elements for any set of values of the parameters R, δ, k, all work was carried out for one set only. The internuclear distance was taken as three Bohr radii, which is the experimental equilibrium distance of the ground state of the neutral molecule. The parameter k appearing in the Slater functions, if determined so as to minimize the energy of ionized lithium, must have the value 2.6875. We have used the value 2.7, which gives an energy for Li^+ differing by 0.00003 atomic unit from the energy obtained by using the optimum value. This energy differs by 1.5 ev from the experimental value because of the very simple wave function used. The choice of the value of the parameter in the outer electron function is not a very critical one since the difference between an exponential having a very good value of δ and the one used can in our case be expanded in a series and absorbed by the coefficients C_I of the general series (4). δ is taken equal to 1.35 since that is the value used in the work on LiH.

We can safely assume, because of the diffuseness of our outer electron function, that there is no real improvement in the wave functions of the inner electrons in the molecule over those in a similar treatment of the atom or ion and therefore that the error in the energy introduced by the use of simple functions for those electrons remains essentially the same in all three cases and will cancel out. For states having normal lithium as one of the dissociation products, it is preferable to take the total energy of the atom as calculated by Wilson[11] (-14.8384Rh) using a four-parameter variational method, since the simplifications made by him in the atomic problem are of the same nature as those made here. We take this value instead of the experimental one because in calculating the difference of molecular and atomic energies, to use an exact value of the atomic energy is to include the large total error of the computed molecular energy in that difference. To obtain atomic energies for the higher states, for which computations are lacking, we have added to the computed core energy the observed ionization energy for the atomic states—a step justified by the considerable accuracy obtainable in computations of ionization energies, even when poor core functions are employed.

The matrix elements have been calculated for all functions with $m=0, 1, 2$ and $j=0, 1, 2, 3$ except the one having $m=2$ and $j=3$. The secular equation is an eleventh order determinantal equation the roots of which are upper bounds to the lowest $^2\Sigma$ energies of LiH^+.

Having calculated the energy at a point, we can obtain the slope of the energy curve with little extra work. Consider $R'=Rq$ where q is nearly one, and let $k'=k/q$ and $\delta'=\delta$. Since the energy of the inner shell is a minimum with respect to k, a small change in the value of k is negligible. Taking the same value of δ at our new point is of no harm since, as we have seen, the exact value of δ is not important. k enters in the expressions for our integrals only in the product kR, which remains unchanged. All integrals of unity contain the factor R^{3n} where n is the number of electrons. For all potential energy integrals the factor is R^{3n-1}, while for all kinetic energy integrals it is R^{3n-2}. R enters in no other way. Since the factor q^{3n} cancels out in obtaining the new energy, we retain the old matrix elements of unity and in the matrix terms for the energy multiply all potential energy integrals by q^{-1} and all kinetic energy terms by q^{-2}. From these new matrix elements the energy at a distance Rdq from the original point can be obtained and used to calculate the slope. In the computations q was taken equal to 1.01 ($dq=0.01$).

From the first root of the secular determinant we find that the lowest state of LiH^+ has a repulsive energy of not over 0.181 ev at a distance of three Bohr radii. The slope at this distance is -0.791 ev per Bohr radius. Details are given in the two tables. Since the energy of repulsion is so small and the slope so large, we conclude, in contradiction to the prediction of Pauling, that the molecule must be stable at larger distances. This can hardly be due to inner shell effects, for James[9] has shown that in Li_2^+, where the behavior of these shells should be essentially the same, they give rise to a repulsion. It would therefore appear that in addition to resonance there may be polarization effects which play an important, or even predominant, part in the formation of a stable one-electron bond.

[11] E. B. Wilson, Jr., J. Chem. Phys. **1**, 210 (1933).

An examination of the importance of the various terms is of interest. The three terms with mj equal to (20), (21), (22) together lower the energy by only 0.006 ev showing that the contributions of terms with higher powers than λ^2 is small. The importance of terms with odd powers of μ is great; (03,13) together lower the energy by 0.163 ev. However, this is less than one-tenth the value of terms with $j=1$. We can safely assume that terms with $j=5$ would not lower the energy by more than 0.02 ev. Similar evidence for terms with $j=4$ gives an even smaller amount for such terms. Therefore we conclude that 0.16 ± 0.02 ev is a close upper bound to the lowest state of LiH^+ at $R=3$. Wilson's calculated value for the ionization energy of Li is too small by about 0.05 ev. If we suppose this difference is due to the simplifications made in the treatment of the inner shell and make a similar correction for LiH^+, we have 0.11 ev as an estimated value of the energy of repulsion.

The next four roots give repulsive energies of 3.885, 4.292, 4.645, and 5.468 ev for the four two-quantum states dissociating into $H^+ + Li\ 2s$, $H^+ + Li\ 2p$, and $H\ 2s$ and $2p + Li^+$, respectively. At infinite separation the first is 1.840 ev below the second which is 0.143 ev below the other two. At $R=3$ the separations are 2.199, 0.497, and 0.823 ev respectively, neglecting the fact that some of the computed energies may be better than others because of better wave functions. The slope for the first of these states has been computed and found to be large (-2.855 ev per Bohr radius) making a stable state at considerably larger distances quite probable.

The first power terms in λ are the most important in these two-quantum states. The first power in λ corresponds to the first power of r which appears in two-quantum atomic functions. An estimate of the decrease in the energy which would be caused by more terms would require the evaluation of many numerical determinants. This has not been done, hence the energies given must be regarded as upper bounds. However, because even in the case of the fifth root there are essentially six coefficients at our disposal, we may expect the computed energies of the two-quantum states, particularly the lower ones, to be rather good.

Normalized coefficients for a simple eight-term function for the lowest state are given in Table I. The coefficients for eleven-term functions for all five states are also given. These latter coefficients have all been calculated from the same determinantal equation and therefore the corresponding wave functions are strictly orthogonal. We define the valence orbitals $U=[1/(\int g^2 dV)^{\frac{1}{2}}]\{\Sigma C_f f + ag\}$, the constant a being so chosen that U is orthogonal to g. If the C_f are so chosen that

TABLE I. *Coefficients of normalized wave functions for LiH^+.* C_{mj} for $R=3$, $\delta=1.35$, $k=2.7$. All the states are repulsive at this distance. W' is the energy referred to isolated H^+ and Li^+ as zero. W_∞' is the value of W' for $R=\infty$.

mj	Lowest State	Lowest State	Second State
00	1.97191	2.21981	−1.78672
01	2.22048	2.29138	0.11061
02	1.17694	1.02505	0.72710
03	1.73098	1.74190	1.44001
10	−0.41862	−0.70165	1.90121
11	−0.36791	−0.45181	−0.62244
12	−0.23984	−0.05147	−2.26936
13	−0.54866	−0.55681	−1.21418
20		0.07181	−0.01359
21		0.02338	−0.21317
22		−0.05034	0.53653
W_∞', Rh	−1.6667	−1.66667	−1.0597
W', Rh	−1.6528	−1.65329	−0.77271
$W'-W_\infty'$ ev	0.187	0.1811	3.885
mj	Third State	Fourth State	Fifth State
00	−7.91415	−9.15988	−0.21866
01	0.65278	1.17803	0.77098
02	17.16824	21.73215	−0.94663
03	−0.79811	0.62136	0.08929
10	8.14604	12.76449	0.42614
11	−2.59954	−2.21312	1.69240
12	−20.09876	−26.57546	1.14955
13	−0.05094	−0.97776	−0.03391
20	−1.94582	−3.61720	−0.63036
21	1.39377	0.66424	−1.20923
22	5.86476	6.67040	1.02214
W_∞', Rh	−0.9273	−0.9167	−0.9167
W', Rh	−0.6102	−0.5736	−0.5127
$W'-W_\infty'$ ev	4.292	4.645	5.468

TABLE II. *Energies of LiH^+ for $R=3.03$.*

	Lowest State	Second State
W_∞'	−1.66007	−1.0531
W'	−1.64844	−0.77244
$W'-W_\infty'$ ev	0.1574	3.799
$\Delta(W'-W_\infty')/\Delta R$	−0.791	−2.855

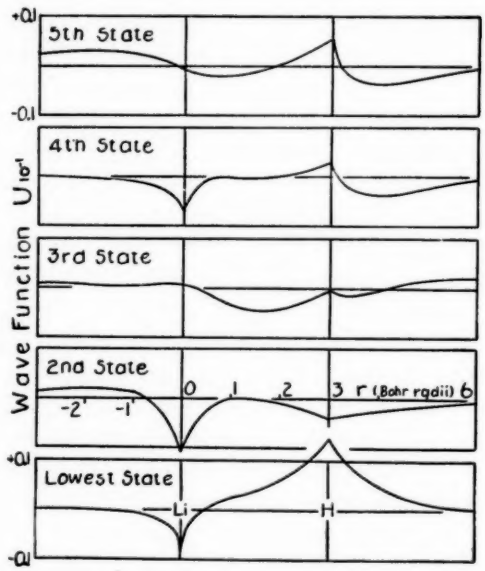

FIG. 1. Valence electron orbitals for the lowest five $^2\Sigma$ states of LiH^+ plotted along the internuclear line. The functions are normalized when multiplied by a factor which is about 0.4. The lowest state dissociates into normal hydrogen and a lithium ion. The four other states are two-quantum states and dissociate into Li $2s+H^+$, Li $2p+H^+$, and Li^++H $2s$ and H $2p$, respectively. Atomic characteristics are noticeable in all the states. These functions are orthogonal to the inner shell functions and to each other.

ψ is normalized, then U is normalized. The U's for different states, like the corresponding ψ's, are orthogonal. In Fig. 1 are graphs showing these functions plotted along the internuclear axis. In the fifth state an antisymmetrical tendency is in evidence.

THE LITHIUM HYDRIDE MOLECULE

For neutral lithium hydride the Hamiltonian of the "clamped" molecule in atomic units is

$$H=\frac{6}{R}-\sum_1^4\left(\nabla_i^2+\frac{6}{r_i}+\frac{2}{s_i}\right)+\sum_{i>j}\frac{2}{r_{ij}}. \qquad (5)$$

We are concerned in this investigation with Σ states only and shall suppose at first that our wave functions can be expressed as the sums of products of orbitals of the type used in the lithium hydride ion. The wave functions, being antisymmetrical in all the coordinates as required by the Pauli principle, must be symmetrical in the space coordinates of the valence electrons for singlet states and antisymmetrical in those coordinates for triplet states. If f and h are two valence electron orbitals, expressions having the proper symmetry are the functions

$$\psi_{fh}=\frac{1}{(48\int g^2dV)^{\frac{1}{2}}}\sum_P(-1)^{\sigma_P}[f(1,\alpha)h(2,\beta)+h(1,\alpha)f(2,\beta)]g(3,\alpha)g(4,\beta) \qquad (6)$$

for singlet states and

$$\psi_{fh}=\frac{1}{(48\int g^2dV)^{\frac{1}{2}}}\sum_P(-1)^{\sigma_P}f(1,\alpha)\times h(2,\alpha)g(3,\alpha)g(4,\beta) \qquad (7)$$

for triplet states. The summations are over all the permutations of the four electrons and σ_P is the number of inversions of the permutations from 1234. This notation is equivalent to the use of determinants. We use it here in preference to determinants because later we shall introduce a function involving the relative coordinates of the two outer electrons and this is easily done with this system of notation.

Let us assume complete wave functions of the form

$$\psi=\sum_{f,\,h}C_{fh}\psi_{fh}, \qquad (8)$$

in which the orbitals are the functions

$$\begin{aligned} f(1,\alpha)&=\lambda_1{}^m\mu_1{}^je^{-\delta\lambda_1}\delta(\alpha,\sigma_1),\\ h(1,\alpha)&=\lambda_1{}^n\mu_1{}^ke^{-\delta\lambda_1}\delta(\alpha,\sigma_1),\\ g(1,\alpha)&=e^{-kr_1}\delta(\alpha,\sigma_1). \end{aligned} \qquad (9)$$

δ, γ and k are parameters independent of $mnjk$ and $\delta(\alpha,\sigma_1)$ is the spin function with the spin coordinate σ_1. The evaluation of matrix elements and adjustment of the parameters C_{fh} is accomplished by the methods used in the treatment of LiH^+.

If we write the Slater wave functions for the H atom and for the outer electron of Li in elliptical coordinates and put $R=3$, we find the parameters in the exponentials to be 1.5 for H and 1.0 for Li. 1.5 and 1.0 are probably good values for our parameters δ and γ. The work of Present on excited states of H_2 shows that the number of terms necessary in the James-Coolidge method is much less for states with nonequivalent electrons if these parameters are taken not the

same. However, because in this case it made possible a marked decrease in the necessary numerical work, δ and γ were given a common value, chosen to be 1.35. It was taken nearer the value for hydrogen since the wave function for lithium is more naturally built up out of powers of λ than is the hydrogen function. As in the problem of the ion, the value of k chosen was 2.70.

For the $^1\Sigma$ ground state the eleven terms ($mnjk$: 1000, 1001, 1002, 1003, 1100, 1101, 1010, 1011, 0000, 2000, 1111) gave the energy $W' = -2.1939$ or a binding energy of 1.82 ev ($W_\infty' = -2.0597$) to be compared with the probable experimental[12] value 2.63 ev. The seven other terms (1102, 1103, 1020, 1030, 0001, 1012, 2001) were tried separately and each gave less than 0.03 ev to the energy. To estimate the value of further terms is hazardous. The changes in the energy caused by the terms tried seem to indicate that the energy improvement obtainable by adding seven or eight more terms to the eleven-term function would not be over 0.15 ev. It is therefore perhaps safe to say that the limiting value for the binding energy obtainable by a function with a large number of terms of the kind here considered is about 2.0 ev or six or seven-tenths of a volt from the experimental value. Coolidge and James found that their simple power series function without the interelectronic terms came within 0.46 ev of the observed value for the ground state of H_2. Present's calculation, gave a difference of about 0.37 ev for an excited two-quantum state of H_2 using a thirteen-term function. James found that for the ground state of Li_2 the difference of 0.5 ev remained between the experimental and computed values for the binding energy after taking eighteen terms of the series.

For the $^3\Sigma$ state an eight-term function made up of the terms (1000, 1001, 1002, 1003, 1101, 1010, 1011, 2000) gave an energy $W' = -1.920$ or a repulsion of 1.89 ev ($W_\infty' = -2.0597$) at a distance of three Bohr radii. Other terms were not tried and the contributions of various terms were not examined. Present, working on a two-quantum $^3\Sigma$ state of H_2, found that a six-term function of this nature but having two different exponential parameters came within 0.08 ev of the experimental value. However he also discovered that when the parameters were given the same value the convergence was very poor. The orbital antisymmetry of the triplet states, which causes the functions to vanish when the valence electrons are near each other, explains why functions not involving the interelectronic distance or the equivalent are better for triplet states than for singlet states and hence why the interelectronic terms are less important in such functions. In our case we can regard the repulsive energy 1.89 ev as an upper bound to the energy which is probably within a few tenths of a volt of the true value.

It is apparent that further improvements of any appreciable amount in the energy for the singlet state must come through the introduction of terms which account for the relative orientation of the valence electrons. We observe that the interelectronic distance is expansible in a series having in it the powers of the cosine of the difference of the azimuthal angles of the two electrons. It is proposed next to investigate the effect of adding terms containing a cosine factor.

In order that our function be single valued, we must introduce a factor which vanishes properly at the poles. Let $P(12)$ denote the function

$$P(12) = M(12)\cos(\phi_1 - \phi_2), \quad M(12) = [(\lambda_1^2 - 1)(1 - \mu_1^2)(\lambda_2^2 - 1)(1 - \mu_2^2)]^{\frac{1}{2}}, \tag{10}$$

where ϕ_1 is the azimuthal angle of electron 1. We can take as additional terms functions of the form

$$\psi_{fhP} = \frac{1}{(48\int g^2 dV)^{\frac{1}{2}}} \sum_P (-1)^{\sigma_P}[f(1,\alpha)h(2,\beta) + h(1,\alpha)f(2,\beta)]P(12)g(3,\alpha)g(4,\beta). \tag{11}$$

[12] The number of observed vibrational levels for the ground state of LiH is only five. For this reason an estimate of the binding energy involves a long extrapolation. Professor Crawford has kindly informed me that the energy we require, using a Morse potential curve and recent experimental data, is about 2.63 ± 0.05 ev. This is more reliable than Nakamura's earlier value of 2.56 ev. See F. H. Crawford and T. Jorgenson, Jr., Phys. Rev. **47**, 932 (1935); G. Nakamura, Zeits. f. Physik **59**, 218 (1930).

$P(12)$ is symmetric with respect to interchange of electrons 1 and 2; hence the proper symmetry conditions are maintained. We define the quantities

$$M(1)=[(\lambda_1^2-1)(1-\mu_1^2)]^{\frac{1}{2}}, \qquad H_0=-\left(\nabla_1^2+\frac{6}{r_1}+\frac{2}{s_1}\right), \qquad H_1=\frac{6}{R}-\sum_1^2\left(\nabla_i^2+\frac{6}{r_i}+\frac{2}{s_i}\right)+\frac{2}{r_{12}},$$

$$(f'f)=\int f'(1)f(1)dV_1, \qquad F=f-[(fg)/(g^2)]g,$$

$$\begin{aligned}
(f'M\backslash fM)&=\int f'(1)M(1)H_0f(1)M(1)dV_1+(4/R^2)(f'f),\\
(f'f/Ph'h)&=\int f'(1)f(1)(2/r_{12})P(12)h'(2)h(2)dV_{12},\\
(f'f/P^2h'h)&=\int f'(1)f(1)(2/r_{12})P^2(12)h'(2)h(2)dV_{12},\\
(h'hM^2)&=\int h'(1)h(1)M(1)^2dV_1.
\end{aligned} \tag{12}$$

The matrix elements of terms involving P with terms not involving P are

$$(F'H'|H|fhP)=[(F'f/PH'h)+(F'h/PH'f)](g^2), \quad (F'H'|1|fhP)=0. \tag{13}$$

We give them for the singlet state only. Matrix elements of P terms with P terms are

$$\begin{aligned}
(f'h'P|H|fhP)=(f'h'P|1|fhP)(g^2)^{-2}&\int g(1)g(2)H_1g(1)g(2)dV_{12}+\tfrac{1}{2}\{[(f'M\backslash fM)(g^2)\\
&+2(f'fM^2/g^2)-(f'g/Pfg)](h'hM^2)+[(f'M\backslash hM)(g^2)+2(f'hM^2/g^2)\\
&-(f'g/Phg)](h'fM^2)+[(h'M\backslash fM)(g^2)+2(h'fM^2/g^2)-(h'g/Pfg)](f'hM^2)\\
&+[(h'M\backslash hM)(g^2)+2(h'hM^2/g^2)-(h'g/Phg)](f'fM^2)\}\\
&+\{(f'f/P^2h'h)+(f'h/P^2h'f)\}(g^2),
\end{aligned} \tag{14}$$

$$(f'h'P|1|fhP)=\tfrac{1}{2}\{(f'fM^2)(h'hM^2)+(f'hM^2)(h'fM^2)\}(g^2).$$

The terms ($1000P$, $1001P$) were added to the eleven-term wave function. The first of the two terms gave an improvement of the energy of 0.09 ev and the second an additional improvement of 0.04 ev. The thirteen-term wave function gave an energy $W'=-2.2036$ or a binding energy of 1.95 ev. It is hardly possible that further terms of this kind would improve the energy by more than 0.1 ev. The failure of the cosine to give greater improvement probably lies in the fact that it does not vary rapidly when the electrons are close together.[13] An exact expansion of the interelectronic distance involves the use of functions with discontinuous derivatives. Higher powers of the cosine or terms having $\cos p(\phi_1-\phi_2)$, p an integer, were not used because their introduction would mean an extension of all the tables and was regarded as impracticable. Terms having $\cos 2(\phi_1-\phi_2)$ would probably have greater value than those used because the cosine of twice the angle varies more rapidly for small angles.

The writer wishes to express his sincere thanks to Professor E. C. Kemble for valuable criticisms on this work. He is deeply indebted and very grateful to Dr. H. M. James for the benefit of many discussions and original suggestions.

[13] That the wave function must depend almost linearly on the interelectronic distance is a result of the work on H_2. Consider also the wave function for H_2, $\psi_0(1-be^{-\beta r_{12}})+\cdots$, where ψ_0 is the first term in the James-Coolidge function. Then if β and b are estimated by fitting this function to their solution, we obtain the approximate values $\beta=0.16$, $b=0.57$. The value of β is small showing the effect to be a long range one. For the He atom a similar estimate can be made using Hylleraas' wave function. We find $\beta=0.18$, $b=0.67$. This suggests that, for two electrons which can be said to be in the same state except for spin, β and b are roughly independent of the nuclear system in which the electrons are moving. They serve to define a sphere of influence of one equivalent electron on the other.

Molecular Constants and Potential Energy Curves for Diatomic Molecules. II

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The potential energy expression $U=e^{-a(r-r_{12})}-C'e^{-a'(r-r_e)}$ previously applied to diatomic molecules containing only first row elements is now applied to other types. For most of them the same value of a (6.0×10^8 cm^{-1}) can be used satisfactorily, the r_{12} values then being additive and depending only on the row of the periodic table in which the atoms occur. Molecules containing but few electrons require different values of a and r_{12}. Values of the equilibrium distance r_e, calculated from ω_e, $\omega_e x_e$ and these constants, are in most cases within 0.02 or 0.03A of the experimentally determined distances (see Table V). The relation between Badger's empirical equation for the calculation of r_e and the equations used in this paper is discussed.

INTRODUCTION

IN the previous paper of this series[1] the assumption that the potential energy of a diatomic molecule (not too far from equilibrium) obeys an expression of the form

$$U(\text{in } 10^{-12} \text{ erg})=e^{-a(r-r_{12})}-C'e^{-a'(r-r_e)} \quad (1)$$

was applied to the band spectrum data for compounds containing only elements in the first row of the periodic table and containing 8 or more electrons. It was found that by taking a (in 10^8 cm^{-1}) as 6.0 and r_{12} (in 10^{-8} cm) as 1.46, for all such molecules in all states but highly excited ones, values of r_e and of various other constants could be calculated which are in quite good agreement with the experimental values. This agreement is taken to indicate that for these molecules the repulsive term in the energy expression is practically independent of the kinds of atoms in the molecule and of the electronic state. The attractive term however varies widely from molecule to molecule and from state to state.

An equation, based on the above energy expression, was given for the calculation of a directly from experimental values of ω_e, $\omega_e x_e$ and r_e. The calculation is quite sensitive to inaccuracies in the assumed constants however; in 10 cases out of 36 an imaginary result is obtained. The values computed in the other cases average close to 6.0, although, as shown in Table I here, there seems to be a trend from lower to higher values as the number of valence electrons (or the sum of the kernel charges) increases. It is quite possible that the relatively poor agreement obtained in calculations of r_e for the C_2 molecule is due to the assumption of too high a value of a.

In this paper the same type of potential function, but, in general, with different values of a and r_{12}, is assumed to hold for other diatomic molecules than those previously considered. On the whole the data are neither so extensive nor so accurate as for the molecules containing only first row elements, hence the calculations of a and r_{12} are less sure. As one consequence, the agreement between calculated and experimental values of r_e, although on the whole satisfactory, is not quite so good as shown in the earlier paper.

THE CALCULATION OF a, r_{12} AND r_e

The results of calculations of rough values of a by the method mentioned in the second paragraph above are collected in Table I. The equation[2] used is

$$a=F/2+(11F^2/12-0.4769M\omega_e x_e)^{\frac{1}{2}}, \quad (2a)$$

where

$$F=\alpha\omega_e/2B_e^2r_e+3/r_e. \quad (2b)$$

M is the reduced mass in atomic weight units. The other symbols have their usual significance. In the case of the hydrogen molecule r_e values were calculated from the r_0 values by the method described in the previous paper, taking $a=5.0$. The assumption of $a=4.0$ or 6.0 for this purpose makes but little difference.

It is evident from the figures in Table I that, if the assumed type of potential function is ap-

[1] Huggins, J. Chem. Phys. **3**, 473 (1935).

[2] Eqs. (15) and (26) of the previous article contain typographical errors. The correct equations are given here as (3a) and (2a).

TABLE I.[3] *Calculated values of a.*

Sum of Kernel Charges	8	9	10	11	12	14
	BeO 5.2	BeF 4.3	CO 6.3	NO 8.4	O_2 6.6	F_2 7.0
	5.7	4.8	5.5	4.6	6.5	
	4.6	BO 5.4	N_2 8.5	6.2		
	C_2 4.8	CN 5.1	7.6	5.9		
		4.8	6.0			
			N_2^+ 5.7			
			6.1			
Average	5.1	4.9	6.5	6.3	6.6	7.0

Sum of Kernel Charges	2	9	10	12	14
	Li_2 1.5	AlO 4.9	P_2 3.5	SO 5.2	Cl_2 5.5
	Na_2 1.2	3.9	6.0	5.3	Br_2 6.3
			TiO 4.6		ICl 7.1
			PbO 2.8		7.0
			SiO 4.7		I_2 2.9
			SiN 4.3		3.5
Average	1.4	4.4	4.3	5.3	5.4

Sum of Kernel Charges	2	3	4	7	8
	NaH 1.7	BeH^+ 3.1	AlH 3.6	HO 6.2	HF 6.1
		3.5			6.0
		BeH 2.7			6.1
		3.1			HCl^+ 2.3
		MgH^+ 1.4			HCl 4.7
		3.5			
		MgH 2.3			
		CaH 2.5			
		2.7			
Average	1.7	2.8	3.6	6.2	5.1

Sum of Kernel Charges	2	3	6	2
	CuH 3.8	ZnH^+ 2.4	BiH 4.7	H_2 7.4
	4.1	4.2	4.7	4.8
	AgH 6.1	CdH^+ 3.1		3.5
	3.8	2.7		6.5
	AuH 2.7	CdH 3.9		6.4
		5.5		
		5.3		
		HgH^+ 5.0		
		2.7		
		HgH 4.1		
Average	4.1	3.9	4.7	5.7

plicable throughout, a gradually increases as the strength of bond (in the normal molecule) increases. Thus, considering hydrides and other molecules separately, a increases as the sum of the kernel charges (or the number of valence electrons) increases. Also, the hydrides of Zn, Cd and Hg (all sub-group elements) seem to have a higher value of a than those of Be, Mg and Ca, in the corresponding main group of the periodic table. There is some indication also of a slightly higher value of a for the first row elements than for corresponding elements in the second and lower rows.

Using these results as a rough guide, calculations of r_{12} from the experimental r_e data have been made for various values of a to find the value or range of values of a for each molecule which leads to nearly the same values of r_{12} for all of its different states for which the data are available. The equations used are as follows:

$$a'=(2.0625a^2+0.7154M\omega_e x_e)^{\frac{1}{2}}-1.750a, \quad (3a)$$

$$C'-C=5.85\times10^{-6}M\omega_e^2/aa', \quad (3b)$$

$$C=(C'-C)/(a/a'-1), \quad (3c)$$

$$r_{12}-r_e=(2.303/a)\log C. \quad (3d)$$

It was found that, as with molecules containing only first row elements, the same value of a could be used successfully for various different molecules. Thus for all hydrides containing from 6 to 8 valence electrons and other diatomic molecules containing from 8 to 14 valence electrons, the assumption of $a=6.0$ leads to satisfactory agreement between the calculated r_{12}

TABLE II. *Values of a and r_{12} used in calculating r_e (Huggins) for Tables III and IV.*

A. Hydrides containing 6 to 8 valence electrons and other molecules containing 8 to 14 valence electrons: $a=6.0$ and $r_{12}=r_1+r_2$

Element	r_1 (or r_2)	*Element*	r_1 (or r_2)
H	0.38×10^{-8} cm	Br	1.11×10^{-8} cm
Be, B C N, O, F	0.73	Te, I	1.26
Al, Si, P, S, Cl	0.96	Pb, Bi	1.25
Ca, Ti	1.00		

B. Hydrides of Zn, Cd, Hg (also Cu, Ag, Au?): $a=4.5$

Molecule	(CuH?), ZnH	(AgH?), CdH	(AuH?), HgH
r_{12}	1.55	1.66	1.66

C. Hydrides of Be, Mg, Ca (also Li, Na, K, Al?): $a=3.5$

Molecule	(LiH?), BeH	(NaH?), MgH, (AlH?)	(KH?), CaH
r_{12}	1.59	1.81	1.92

D. Li_2: $a=2.0$. $r_{Li_2}=2.54$

E. Na_2, (K_2?): $a=1.65$. $r_{Na_2}=3.01$, $r_{K_2}=3.44$ (?)

F. H_2: $a=4.5$, $r_{H_2}=1.01$ or $a=5.0$, $r_{H_2}=0.95$ or $a=6.0$, $r_{H_2}=0.90$.

[3] Most of the data used in the preparation of Tables I, III and IV were obtained from Jevons, *Report on Band Spectra of Diatomic Molecules* (University Press, Cambridge, England, 1932). Results are included for all molecular states for which he gives the requisite data (not in parenthesis), except that the 26 states for which the data lead to imaginary values of a are omitted from Table I. For references, other than to Jevons, for work on molecules containing only Be, B, C, N, O and F, see the previous paper of this series. In Tables III and IV, although the values of r_e (calc.) $-r_e$ (exp.) are given to 3 decimal places (except when less are given for r_e (exp.), the last figure may be in error by 2 or 3 units, as most of the calculations were made by slide rule.

TABLE III.[2] *Comparisons of calculated and experimental equilibrium distances.*

FORMULA	ω_e (exp.) (cm^{-1})	r_e (exp.) (10^{-8} cm)	r_e(calc.) $-r_e$(exp.) (Huggins) (10^{-8} cm)	r_e(calc.) $-r_e$(exp.) (Badger) (10^{-8} cm)	REFERENCE
C_2	1832.45	1.251	−0.201	−0.031	
	1792.55	1.261	−0.060	−0.033	
	1608.31	1.315	−0.031	−0.045	
	1641.55	1.308	−0.028	−0.047	
N_2^+	2419.84	1.071	−0.059	+0.036	
	2207.19	1.113	−0.004	+0.020	
N_2	1732.84	1.201	+0.002	+0.011	
	1692.28	1.209	+0.011	+0.012	
	1460.39	1.289	−0.025	−0.013	
	2359.60	1.092	+0.008	+0.022	
O_2^+	898.9	1.41	−0.02	+0.06	
	1876.4	1.14	−0.02	+0.02	
O_2	710.14	1.599	−0.112	+0.005	
	1432.615	1.223	+0.009	+0.035	
	1584.91	1.204	+0.016	+0.017	
F_2	977	1.45	—	−0.095	
	1139.8	1.28	+0.021	+0.036	
CN	2164.15	1.148	−0.042	+0.003	
	1788.66	1.236	−0.010	−0.020	
	2068.79	1.169	+0.007	−0.003	
BeO	1006	>1.47	>−0.007	<+0.027	
	1370.81	1.358	+0.013	−0.014	
	1127.77	1.468	−0.034	−0.030	
	1486.87	1.327	−0.005	−0.017	
BO	1280.3	1.301	+0.051	+0.046	
	1297.13	1.343	+0.010	−0.002	
	1260.42	1.342	+0.011	+0.013	
	1940.26	1.203	+0.011	−0.017	
	1885.44	1.202	+0.012	−0.006	
CO^+	1722.1	1.16	−0.03	+0.06	
	1564.53	1.24	+0.01	+0.01	
	2212	1.11	+0.02	+0.03	
CO	2182	1.118	—	+0.022	
	1516.7	1.232	−0.001	+0.035	
	1739.3	1.202	−0.006	+0.014	
	2169.32	1.127	+0.017	+0.014	
NO	2355	1.07	0.000	+0.034	
	1038.6	1.413	−0.003	+0.001	
	2375.3	1.060	+0.002	+0.043	
	1906.5	1.146	+0.008	+0.023	
BeF	1172.6	1.390	+0.015	+0.012	
	1265.6	1.357	+0.021	+0.010	
HO	3182.5	1.009	−0.015	+0.021	
HF	4123.12	0.915	+0.008	+0.013	4
HCl^+	1603	1.528	−0.027	+0.137	
HCl	2989.68	1.272	+0.009	+0.026	
HBi	1716.94	1.784	−0.008		
	1678.16	1.804	−0.018		
CP	1239.67	1.558	−0.005	−0.017	5
	1061.99	1.667	−0.055	−0.083	5
	836.32	1.685	+0.007	+0.011	5
CS	1072.3	1.56	+0.01	+0.02	6
	1285.1	1.53	+0.01	−0.02	6
SiN	1031.01	1.576	−0.087	+0.005	
	1151.68	1.568	−0.004	−0.032	
PN	1337.24	1.487	+0.015	−0.014	5
	1103.09	1.542	+0.021	+0.003	5
AlO	868.15	1.663	+0.005	−0.021	
	977	1.614	−0.016	−0.026	
SiO	848.1	1.618	+0.037	+0.031	7
	1240.5	1.505	+0.020	−0.014	
SO	628.7	1.769	−0.025	+0.024	
	1123.73	1.489	+0.056	+0.030	
SiF	716.5	1.595	+0.076	+0.111	8
	865.0	1.595	+0.041	+0.021	8
P_2	475.22	2.115	−0.092	+0.066	9
	780.43	1.856	−0.001	−0.009	
S_2	727.4	1.840	+0.030	+0.029	10
Cl_2	261.1	2.42	−0.27	+0.02	
	564.9	1.983	−0.066	−0.023	
Br_2	165.39	2.65	−0.15	+0.09	
	323.86	2.28	+0.01	+0.01	
Te_2	250.9	2.85	−0.24	−0.30	
I_2	128.0	3.010	−0.197	−0.005	
	214.26	2.660	−0.004	−0.017	
ICl	212.3	2.644	−0.117	+0.046	
	384.6	2.310	−0.015	−0.015	
CaO	705.8	1.82	−0.09	−0.04	11
	718.5	1.74	0.00	+0.03	
TiO	837.86	1.690	−0.016	+0.003	
	1008.12	1.617	−0.004	+0.003	
PbO	530.6	2.042	+0.034	+0.001	
	451.7	2.089	+0.011	+0.042	
	722.3	1.918	+0.020	−0.021	
Li_2	269.69	2.93	0.00	+0.07	
	253.2	3.11	−0.01	−0.01	
	351.60	2.67	+0.01	−0.04	
Na_2	123.79	3.404	+0.033	+0.098	
	115.60	3.663	−0.008	−0.058	
	159.23	3.070	−0.001	+0.084	
K_2	75.00	4.22	−0.09?	−0.02	
	92.64	3.91	0.00?	−0.07	
BeH^+	1476.1	1.603	+0.023	−0.089	
	2220.0	1.310	−0.030	−0.077	
BeH	2087.6	1.330	−0.016	−0.059	
	2058.5	1.340	+0.005	−0.060	
MgH^+	1138.4	2.008	−0.012	−0.049	
	1702.2	1.649	−0.001	−0.016	
MgH	1603.45	1.68	0.00	0.00	
	1493.45	1.73	−0.01	0.00	
CaH	1448	1.85	+0.03	−0.04	
	1147.5	2.61	−0.62	−0.60	
	1285	1.95	+0.03	−0.04	
	1333	1.99	−0.03	−0.11	
	1316.7	2.02	−0.05	−0.13	
LiH	287.4?	2.5	+0.2?	+1.4	
	1406.1	1.6	0.0?	0.0	
NaH	345.20	3.0	−0.3?	+0.6	
AlH	1680.6	1.644	+0.044?	−0.003	
ZnH^+	1365	1.71	+0.01	+0.14	
	1916	1.51	0.00	+0.10	
CdH^+	1250	1.86	+0.02		
	1773	1.66	0.00		
CdH	874.1	2.378	−0.37		
	1749.8	1.660	+0.01		
	1430.7	1.754	−0.02		
HgH^+	1647	1.69	−0.09		
	2016	1.59	0.00		
HgH	2063.2	1.580	0.00		
	1432.7	1.729	−0.22		
CuH	1699.9	1.568	−0.017?	+0.120	
	1939.9	1.460	+0.051?	+0.142	
AgH	1663.6	1.638	−0.095?		
	1760.0	1.614	+0.054?		
AuH	1690	1.67	−0.08?		
	2302	1.52	+0.01?		

values. Moreover, these r_{12} values were nearly the same for practically all compounds satisfying these requirements which have the same distribution of kernel electrons, e.g., for all molecules composed of one first row element and one second row element. In addition there is ap-

[4] Kirkpatrick and Salant, Phys. Rev. **48**, 945 (1935).

[5] Bärwald, L. Herzberg and G. Herzberg, Ann. d. Physik **20**, 569 (1934).

[6] Crawford and Shurcliff, Phys. Rev. **45**, 860 (1934).

[7] Jevons gives r_0 but not r_e. To obtain the latter, use was made of the rough value of α computed by means of Eq. (21) of the previous paper.

[8] The r_0 values given for the SiF molecule by Jevons are divided by $\sqrt{2}$ to accord with the conclusions of Badger and Blair, Phys. Rev. **47**, 881 (1935). The equilibrium distance r_e was then calculated from r_0 as outlined in reference 7.

[9] G. Herzberg, Ann. d. Physik (5) **15**, 677 (1932); Phys. Rev. **40**, 313 (1932).

[10] The value of r_e used is from Badger, Phys. Rev. **46**, 1025 (1934). Van Dijk and Lameris, Physica **2**, 785 (1935), obtain $r_0=1.73$A, which is certainly too low, if the values of ω_e and $\omega_e x_e$ are correct. If the data on P_2 and Cl_2 are not in error, calculations of the sort made in this paper lead one to expect a value of about 1.90A. Maxwell, Hendricks and Mosley, Phys. Rev. **49**, 199 (1936), obtain 1.94 ± 0.03A for the internuclear distance in S_2 molecules by electron diffraction.

[11] Brodersen, Zeits. f. Physik **79**, 613 (1932).

proximate additivity of these r_{12} values. From the set of "basic radii" given in Table II one can, by addition, calculate r_{12} values and from these and the experimental constants ω_e and $\omega_e x_e$ compute equilibrium distances r_e for a large number of molecules. The degree of agreement with the experimental equilibrium distances is shown in Table III.

It should be mentioned that some of the data on which the calculation of the radii in Table II are based are meager and inadequate. In many cases also the data are for highly excited states, for which, in considering only the first row elements, poor agreement was found. Slightly better agreement between calculated and experimental values of r_e could also be obtained if one gave up the assumption of additivity or used different values of a for different molecules. For present purposes at least, with the limited data available, the usefulness of the additivity and constancy of a approximations would seem to make their use advisable.

To obtain reasonable agreement between the r_{12} values calculated for different states of other hydride molecules and of molecules of the alkali metals, smaller values of a have to be assumed. The values chosen and the r_{12} values resulting therefrom are listed in Table II. The equilibrium distances computed from these are compared with the experimentally determined distances in Table III. Again the agreement is satisfactory.

For the hydrogen molecule the results of calculations of r_{12} assuming three different values of a are given (Table IV). There is really little to choose between them, the general agreement being about equally good in each case. Whether the large disagreement shown, for any choice of a, by some states is due to experimental errors or is an indication that the assumed potential expression is far from accurate for these cases, it does not seem possible at present to decide.

TABLE IV.[2] *Comparison of calculated and experimental equilibrium distances for H_2.*

State	ω_e(exp.) (cm^{-1})	a (cm^{-1})	r_e(exp.) (10^{-8} cm)	r_e(calc.)−r_e(exp.) (Huggins) $a=4.5$ $r_{12}=1.01$ (10^{-8}cm)	$a=5.0$ $r_{12}=0.95$ (10^{-8}cm)	$a=6.0$ $r_{12}=0.90$ (10^{-8}cm)	(Badger) (10^{-8} cm)
$1s\sigma 6p\pi\ ^3\Pi_u$	2293	1.6*	1.052	+0.013	+0.003	+0.008	+0.037
$1s\sigma 5p\pi\ ^3\Pi_u$	2309	1.6*	1.052	+.009	+.000	+.006	+.033
$1s\sigma 4p\pi\ ^3\Pi_u$	2336.5	1.6*	1.051	+.003	−.005	+.003	+.026
$1s\sigma 3p\pi\ ^3\Pi_u$	2372.53	2.72	1.035	+.003	−.001	+.009	+.030
$1s\sigma 3p\sigma\ ^3\Sigma^+$	2197	2.2*	1.103	−.031	−.038	−.033	+.017
$1s\sigma 2p\pi\ ^3\Pi_u$	2463	1.9*	0.96	+.06	+.06	+.07	+.08
$1s\sigma 2s\sigma\ ^3\Sigma_g^+$	2664.61	1.650	0.986	−.003	−.001	+.018	+.002
$(3^1M)\ ^1\Sigma_g$	2209	3.2*	1.6	−.5	−.5	−.5	−.5
$1s\sigma 3d\sigma\ ^1\Sigma_g^+$	2538	2.1*	1.04	−.10	−.08	−.05	−.02
$1s\sigma 3d\pi\ ^1\Pi_g$	2252.90	2.1*	1.07	−.02	−.02	−.01	+.04
$1s\sigma 3d\sigma\ ^1\Sigma_g^+$	2455.45	2.1*	1.05	−.09	−.07	−.04	−.01
$2p\sigma 3p\sigma\ ^1\Sigma_g$	2245.4	3.5*	1.74	−.60	−.63	−.64	−.63
$1s\sigma 2p\pi\ ^1\Pi_u$	2446.5	1.2	1.05	−.03	−.03	−.02	−.01
$1s\sigma 2p\sigma\ ^1\Sigma_u^+$	1357.266	1.94	1.276	+.06	+.02	−.02	+.259
$1s\sigma^2\ ^1\Sigma_g^+$	(4371)	2.9	0.740	−.031	+.010	+.079	

* The values of a marked with an asterisk were calculated by means of Eq. (24) of the earlier paper in this series.

TABLE V. *Summary of deviations of calculated from experimental values of r_e.*

	±(r_e(calc.−r_e(exp.)) 0.025A or less	0.026A to 0.050A	0.051A to 0.150A	>0.150A	Total
Huggins	{87	21	19	14	141
Badger	{78 63	21 33	15 24	12 6	126* 126*

* All those for which Badger gives the necessary constants.

COMPARISON WITH BADGER'S EQUATION

Badger[12] has shown that the equilibrium distances for most diatomic molecules in most of their electronic states for which the data are known may be calculated approximately by the simple empirical equation

$$r_e = d_{ij} + C_{ij}^{\frac{1}{3}}/k_e^{\frac{1}{3}}, \tag{4}$$

in which k_e is the "bond force constant" and C_{ij} and d_{ij} are constants characteristic of the rows of the periodic table in which the two elements occur. As may be seen from Tables III, IV and V, the agreement obtained by using this equation with the constants he gives is nearly as good as by the method described in this paper. In most of the cases of marked disagreement between the experimental value of the equilibrium distance and that calculated by one of the two methods, there is also a similar disagreement when the calculation is made by the other method.

The relation between the two methods can be shown in the following way. The force constant k_e, in megadynes per centimeter (the unit used by Badger) is related to ω_e, in cm^{-1}, by the equation

$$k_e = 5.85\times 10^{-8} M\omega_e^2. \tag{5}$$

This may be combined with Eqs. (3a), (3c) and (3d) to give

$$r_e = r_{12} - \frac{2.303}{a}\log\left(\frac{100k_e}{a^2 - aa'}\right), \tag{6a}$$

[12] Badger, J. Chem. Phys. **2**, 128 (1934); **3**, 710 (1935).

which is equivalent to

$$r_e=\left[r_{12}+\frac{2.303}{a}\log\left(\frac{a^2-aa'}{100}\right)-K_{ij}\right]+\left[K_{ij}-\frac{2.303}{a}\log k_e\right], \quad (6b)$$

where K_{ij} is any distance. Now we have shown that a is practically a constant (usually 6) for diatomic molecules of the same ij class—composed of elements from the same two rows of the periodic table—provided the sums of the kernel charges are not too different. Also (see column 7 of the table in the previous paper) a' is almost invariably small compared with a; moreover, for most states of most molecules of the same ij type, a' has *roughly* the same value. Therefore (a^2-aa') is the difference between a relatively large number (36) and a small, roughly constant number (approximately 6 for *1, 1* type molecules, zero for *1, 2* type molecules, etc.). The quantity in the first set of brackets in Eq. (6b) is thus nearly constant, for a given type, no matter what value K_{ij} has. By choosing a suitable value for K_{ij} the quantity $(K_{ij}-(2.303/a)\log k_e)$ can be made closely equal to $(C_{ij}^{\frac{1}{2}}/k_e^{\frac{1}{2}})$ over quite a range of values of k_e. Making such a choice for the range of k_e values of a given ij type, it is seen that Eq. (6b) is approximately equivalent to Eq. (4).

The relation between Badger's constants d_{ij} and $C_{ij}^{\frac{1}{2}}$ is readily obtained from a comparison of these equations. Equating corresponding portions,

$$K_{ij}=r_{12}+\frac{2.303}{a}\log\left(\frac{a^2-aa'}{100}\right)-d_{ij} \quad (7)$$

and

$$K_{ij}=\frac{C_{ij}^{\frac{1}{2}}}{k_e^{\frac{1}{2}}}+\frac{2.303}{a}\log k_e. \quad (8)$$

Eliminating K_{ij} we obtain

$$d_{ij}=r_{12}+\frac{2.303}{a}\log\left(\frac{a^2-aa'}{100k_e}\right)-\frac{C_{ij}^{\frac{1}{2}}}{k_e^{\frac{1}{2}}}. \quad (9)$$

For molecules of first row elements, average values of k_e and a' (neglecting the few high energy states giving poor agreement between experimental equilibrium distances and those calculated by Eq. (3)) are 1.28 and 1.23, respectively. Substituting these and the values 1.46 for r_{12} and 6.0 for a, we calculate

$$d_{1,1}=1.214-0.92C_{1,1}^{\frac{1}{2}}. \quad (10)$$

This equation is nearly satisfied by Badger's values of 0.68 and 0.571 for $d_{1,1}$ and $C_{1,1}^{\frac{1}{2}}$, respectively. Similar calculations for other ij types lead to similar results.

Conclusion

It is evident from the agreement between calculated and experimental equilibrium distances that the type of potential expression used is not a bad approximation for values of r not too far from r_e. The approximate equivalence of the constants a and r_{12} in the repulsive term for different molecules composed of atoms of the same two rows of the periodic table (having not too different a sum of kernel charges) makes this type of potential equation especially useful. In this paper application has been made only to the calculation of r_e values, but other molecular constants can also be roughly calculated by the methods described in the previous paper. The approximate additivity of r_{12} values is useful in extending the calculations to other types of molecule.

Undoubtedly in many of the molecules dealt with in this paper the true variation of potential energy with distance is more accurately approximated by a function of the chosen type with somewhat different values of a and r_{12} than those used here, but with the present data one cannot easily (if at all) determine the best values; also the usefulness of the function for purposes of prediction is greatest if the same values of these constants can be used successfully with large groups of molecules and states.

If the prediction of r_e were the only useful result of the potential energy expression employed in this paper, little advantage could be claimed over the empirical equation proposed by Badger. From the author's relation however, various other unknown or doubtful molecular constants can also be calculated. In addition, the whole potential energy curve can be obtained with reasonable accuracy from a minimum of data.

The Vibration-Rotation Energy Levels of Polyatomic Molecules

II. Perturbations Due to Nearby Vibrational States

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The use of the Wang secular equation for the interpretation of the rotational structure of a vibration-rotation band of an asymmetrical top molecule is not justified if either of the vibrational states involved in producing the band is perturbed by another vibrational state of nearly the same energy. The present paper discusses the conditions under which such a perturbation is to be expected and gives the secular equation which should be used instead of the Wang determinant in case the perturbation is important. This equation assumes a somewhat simpler form when applied to orthorhombic molecules, in which case it involves only one parameter in addition to the three moments of inertia.

INTRODUCTION

IN a previous paper[1] (hereafter called I) the Hamiltonian operator for the rotation and vibration of a semirigid polyatomic molecule was obtained and applied to the problem of the energy levels of asymmetrical top molecules. It was stated, however, that the perturbation technique used is not valid when the vibrational state of interest interacts with another vibrational state of nearly the same energy. The latter special case will be treated in this paper.

THE HAMILTONIAN OPERATOR

A lower degree of approximation will be used than in I, inasmuch as the phenomenon to be treated is more complicated. The results are, however, probably sufficiently accurate for present practical needs. If in the future it should become important to have higher approximations, these can be obtained by an extension of the methods employed in I.

The quantities $\mu_{\alpha\beta}$ and h_α which occur in Eq. (33) of I will therefore be replaced by their approximate values, with the result that the Hamiltonian operator $\mathbf{H}$ can be written in the form used by several other investigators;[2] namely,

$$\mathbf{H}=\tfrac{1}{2}(\mathbf{P}_x^2/A_0+\mathbf{P}_y^2/B_0+\mathbf{P}_z^2/C_0)-(p_x\mathbf{P}_x/A_0+p_y\mathbf{P}_y/B_0+p_z\mathbf{P}_z/C_0)+\mathfrak{V}, \quad (1)$$

in which $\mathbf{P}_x$, $\mathbf{P}_y$, and $\mathbf{P}_z$ are the operators for the components of the total angular momentum along the three moving axes x, y, and z fixed to the molecule; p_x, p_y, and p_z are the operators for the corresponding components of vibrational angular momentum; A_0, B_0, and C_0 are the equilibrium moments of inertia; $\mathfrak{V}$ is the operator for the vibrational energy.

SECULAR EQUATION FOR THE GENERAL CASE

Part of the infinite secular equation for this problem (or also the matrix for $\mathbf{H}$) in terms of the functions $\psi_R\psi_V$ is represented in Fig. 1, ψ_R being a solution of the wave equation for the symmetrical rigid top while ψ_V is a solution of $\mathfrak{V}\psi_V=W_V\psi_V$. ψ_R is a function of the rotational coordinates only and involves the quantum numbers R, whereas ψ_V is a function of the internal coordinates and involves the quantum numbers V.

The doubly shaded blocks, representing groups of elements diagonal in V but having all values of R, R', come from the purely rotational and purely vibrational parts of $\mathbf{H}$ in Eq. (1), while the singly shaded and unshaded blocks come from the coupling terms $-p_x\mathbf{P}_x/A_0$, etc. These coupling terms do not contribute to the elements diagonal in V because[3]

$$\int\psi_V p_x\psi_V d\tau=0, \quad \text{etc.}, \quad (2)$$

for nondegenerate states ψ_V. The coupling terms may be regarded as a perturbation whose first-order effect vanishes. Ordinarily, the second-order effect will be fairly small. If, however, two states V and V' have energies W_V and $W_{V'}$

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[1] E. B. Wilson, Jr. and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).

[2] For a full list of references, see footnote 2 of I.

[3] For proof see I, footnote 11 and associated text.

rather near one another, the second-order effect will become large, and in fact, the use of ordinary perturbation theory will become impractical. This case can be treated by retaining the elements connecting the states V and V' and neglecting all other nondiagonal terms. Thus in Fig. 1, the unshaded blocks will be neglected but the singly shaded elements, which connect two states of nearly the same energy, will be retained. The secular equation can then be factored into the shaded blocks. The energy levels of the two interacting vibrational states will be determined by the double-size, horizontally shaded part of Fig. 1.

The matrix elements for

$$(P_x^2)_{R,\,R'}=\int\psi_R^*\mathbf{P}_x^2\psi_{R'}d\tau,$$

etc., are known[4] to be

$$\begin{aligned}(P_x^2)_{J,\,K,\,M;\,J,\,K,\,M}&=(P_y^2)_{J,\,K,\,M;\,J,\,K,\,M}\\&=(h^2/8\pi^2)[J(J+1)-K^2],\\(P_z^2)_{J,\,K,\,M;\,J,\,K,\,M}&=K^2(h^2/4\pi^2),\\(P_x^2)_{J,\,K,\,M;\,J,\,K\pm2,\,M}&=-(P_y^2)_{J,\,K,\,M;\,J,\,K\pm2,\,M}\\&=(h^2/16\pi^2)[(J\mp K)(J\mp K-1)\\&\quad\times(J\pm K+1)(J\pm K+2)]^{\frac{1}{2}},\end{aligned}\tag{3}$$

all other elements vanishing. J, K and M are the quantum numbers for the symmetrical top (represented by R above). With the use of these quantities the secular equation can be obtained. It has the following nonzero elements:[5]

$$\begin{aligned}(K,\,V|K,\,V)&=K^2+\sigma_V-\sigma;\\(K,\,V'|K,\,V')&=K^2+\sigma_{V'}-\sigma;\\(K,\,V|K\pm2,\,V)&=(K,\,V'|K\pm2,\,V')\\&=\tfrac{1}{2}b\{[J^2-(K\pm1)^2][(J+1)^2-(K\pm1)^2]\}^{\frac{1}{2}};\\(K,\,V|K,\,V')&=-(K,\,V'|K,\,V)=iG_zK;\\(K,\,V|K\pm1,\,V')&=-(K,\,V'|K\pm1,\,V)\\&=(iG_x\pm G_y)\tfrac{1}{2}[(J\mp K)(J\pm K+1)]^{\frac{1}{2}}.\end{aligned}\tag{4}$$

[4] See, for example, O. Klein, Zeits. f. Physik **58**, 730 (1929).

[5] As in Wang's solution of the rigid asymmetrical top problem (Phys. Rev. **34**, 243 (1929)), which this treatment somewhat resembles, the secular equation factors into equations for each value of J and M; i.e., $\mathbf{H}$ is diagonal in J and M. It is not diagonal, however, in K.

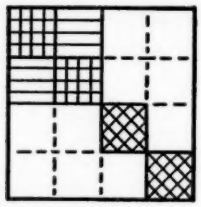

FIG. 1. Part of the infinite secular equation for $\mathbf{H}$, divided into vibrational blocks. Doubly shaded areas are diagonal in V. Singly shaded areas connect two vibrational states of nearly the same energy.

This secular equation has $2(2J+1)$ rows and columns, which are labeled by K and V, the former having the values J, $J-1$, $\cdots$, $-J+1$, $-J$, the latter the values V and V'. Consequently it is of degree $2(2J+1)$ in σ. The symbols have the meaning

$$\begin{aligned}a&=(1/2c)(1/A_0+1/B_0),\\b&=(1/2c)(1/A_0-1/B_0),\\c&=1/C_0-\tfrac{1}{2}(1/A_0+1/B_0),\\\sigma&=(8\pi^2/h^2c)W-J(J+1)a,\quad\sigma_V=(8\pi^2/h^2c)W_V,\\G_x&=(2/cA_0)\sum_{ikl}(m_{ik}n_{il}-m_{il}n_{ik})I_{kl},\\G_y&=(2/cB_0)\sum_{ikl}(n_{ik}l_{il}-n_{il}l_{ik})I_{kl},\\G_z&=(2/cC_0)\sum_{ikl}(l_{ik}m_{il}-l_{il}m_{ik})I_{kl},\\I_{kl}&=\int\psi_{V'}{}^*Q_k(\partial/\partial Q_l)\psi_V d\tau.\end{aligned}\tag{5}$$

The coefficients l_{ik}, m_{ik}, n_{ik} define the normal coordinates Q_k by means of the relation

$$Q_k=\sum_{i=1}^{3N}(l_{ik}\xi_i+m_{ik}\eta_i+n_{ik}\zeta_i),\tag{6}$$

in which ξ_i, η_i, and ζ_i are the displacements from equilibrium in the x, y, z directions, respectively, of the ith atom, multiplied by the square root of the mass of that atom. If the harmonic oscillator approximation is valid, ψ_V and $\psi_{V'}$ can be written down and I_{kl} evaluated (see Eq. 9).

SECULAR EQUATION FOR ORTHORHOMBIC MOLECULES

Molecules of orthorhombic symmetry (i.e., point groups $\mathbf{V}$, $\mathbf{V}_h$ and $\mathbf{C}_{2V}$), a classification which includes most asymmetrical top molecules

of interest, such as water, formaldehyde and ethylene, allow additional simplification. For this symmetry, p_x, p_y and p_z each has distinctive symmetry properties (irreducible representations) which are different from the complete symmetry of the molecule. Also, G_x, for example, vanishes unless $\psi_{V'}\psi_V$ has the same symmetry properties as p_x. Therefore, for a given pair V, V', at most one of G_x, G_y and G_z, will be different from zero. In case $\psi_{V'}\psi_V$ has a symmetry different from that of each of p_x, p_y and p_z, this type of perturbation will vanish completely.

Furthermore, in each of the three cases ($G_x\neq 0$, $G_y\neq 0$, or $G_z\neq 0$) in which the two levels may perturb one another, it is possible to factor the secular equation into four equations of lower degree. Below are given the transformations which bring about the factoring and the nonzero elements of the factors themselves for the three cases.

$$\begin{aligned}
&\text{Let } \Lambda_K=2^{-\frac{1}{2}}(\psi_{JKM}+\psi_{J-KM})\psi_V \quad (K>0),\\
&\Lambda_0=\psi_{J0M}\psi_V,\\
&\Gamma_K=2^{-\frac{1}{2}}(\psi_{JKM}+\psi_{J-KM})\psi_{V'} \quad (K>0),\\
&\Gamma_0=\psi_{J0M}\psi_{V'},\\
&\phi_K=2^{-\frac{1}{2}}(\psi_{JKM}-\psi_{J-KM})\psi_V \quad (K>0),\\
&\Omega_K=2^{-\frac{1}{2}}(\psi_{JKM}-\psi_{J-KM})\psi_{V'} \quad (K>0).
\end{aligned} \tag{7}$$

These functions, together with the specification of K as even or odd, will serve to factor each of the three cases, different combinations occurring in each case.

The elements out of which the various factors of the secular equation are constructed are given below.

$$\begin{aligned}
&(\Lambda_K|\Lambda_K)=K^2+\delta_{K,1}\tfrac{1}{2}bJ(J+1)+\sigma_V-\sigma\\
&\qquad\qquad (K=0 \text{ included}),\\
&(\phi_K|\phi_K)=K^2-\delta_{K,1}\tfrac{1}{2}bJ(J+1)+\sigma_V-\sigma(K>0),\\
&(\Lambda_2|\Lambda_0)=(\Lambda_0|\Lambda_2)=2^{-\frac{1}{2}}b[(J^2-1)(J^2+2J)]^{\frac{1}{2}},\\
&(\Lambda_K|\Lambda_{K\pm 2})=(\phi_K|\phi_{K\pm 2})=\tfrac{1}{2}b\{[J^2-(K+1)^2]\\
&\quad\times[(J+1)^2-(K\pm 1)^2]\}^{\frac{1}{2}} \quad (K\pm 1\neq 1),\\
&(\Lambda_K|\Omega_K)=-(\Omega_K|\Lambda_K)=iG_zK \quad (G_z\neq 0),\\
&(\Lambda_0|\Gamma_1)=-(\Gamma_1|\Lambda_0)=2^{-\frac{1}{2}}iG_x[J(J+1)]^{\frac{1}{2}}\\
&\qquad\qquad (G_x\neq 0),\\
&(\Lambda_K|\Gamma_{K\pm 1})=-(\Gamma_K|\Lambda_{K\pm 1})=(\phi_K|\Omega_{K\pm 1})\\
&\quad=-(\Omega_K|\phi_{K\pm 1})=\tfrac{1}{2}iG_x[(J\mp K)(J\pm K+1)]^{\frac{1}{2}}\\
&\qquad\qquad (G_x\neq 0) \quad (K>0),\\
&(\Lambda_0|\Omega_1)=(\Omega_1|\Lambda_0)=2^{-\frac{1}{2}}G_y[J(J+1)]^{\frac{1}{2}} \quad (G_y\neq 0),\\
&(\Lambda_K|\Omega_{K\pm 1})=(\Omega_{K\pm 1}|\Lambda_K)\\
&\quad=\pm\tfrac{1}{2}G_y[(J\mp K)(J\pm K+1)]^{\frac{1}{2}}\\
&\qquad\qquad (G_y\neq 0) \quad (K>0).
\end{aligned} \tag{8}$$

Elements in which Γ_K replaces Λ_K and ϕ_K replaces Ω_K are obtained from the above by interchanging V and V' wherever they appear. $\delta_{K,1}$ is unity if $K=1$, zero otherwise.

The combinations of functions which lead to the individual factors are given below. The degree of each factor is also given.

Case $G_x\neq 0$, $G_y=G_z=0$

(a) Λ_K ($K=0, 2, 4, \cdots$) and Γ_K ($K=1, 3, 5, \cdots$). Degree: $J+1$.
(b) Γ_K ($K=0, 2, 4, \cdots$) and Λ_K ($K=1, 3, 5, \cdots$). Degree: $J+1$.
(c) Ω_K ($K=2, 4, \cdots$) and ϕ_K ($K=1, 3, 5, \cdots$). Degree: J.
(d) ϕ_K ($K=2, 4, \cdots$) and Ω_K ($K=1, 3, 5, \cdots$). Degree: J.

Case $G_y\neq 0$, $G_x=G_z=0$

(a) Λ_K ($K=0, 2, 4, \cdots$) and Ω_K ($K=1, 3, 5, \cdots$). Degree: $J+1$.
(b) Ω_K ($K=2, 4, \cdots$) and Λ_K ($K=1, 3, 5, \cdots$). Degree: J.
(c) Γ_K ($K=0, 2, 4, \cdots$) and ϕ_K ($K=1, 3, 5, \cdots$). Degree: $J+1$.
(d) ϕ_K ($K=2, 4, \cdots$) and Γ_K ($K=1, 3, 5, \cdots$). Degree: J.

Case $G_z\neq 0$, $G_x=G_y=0$

(a) Λ_K and Ω_K ($K=0, 2, 4, \cdots$). Degree: $J+1$ for J even, J for J odd.
(b) Λ_K and Ω_K ($K=1, 3, 5, \cdots$). Degree: J for J even, $J+1$ for J odd.
(c) Γ_K and ϕ_K ($K=0, 2, 4, \cdots$). Degree: $J+1$ for J even, J for J odd.
(d) Γ_K and ϕ_K ($K=1, 3, 5, \cdots$). Degree: J for J even, $J+1$ for J odd.

The matrix elements between functions listed under different letters for each case above are all zero; hence each letter represents a factor of the secular equation.

Qualitative Conclusions

It can be seen from the mathematical treatment that certain additional conditions must be satisfied before two vibrational states V and V' will perturb one another strongly, even when they are close together in energy. The first condition is that $\psi_{V'}\psi_V$ have the same symmetry properties as one or more of the angular momenta p_x, p_y and p_z. A second condition is that I_{kl} shall not be too small for some pair of normal coordinates kl. This requires, since ψ_V is approximately given by harmonic oscillator functions, that the two states V and V' differ in two and only two of their vibrational quantum numbers v_k and that these two quantum numbers change by one unit from V to V'. Since $W_V \cong W_{V'}$, this practically limits the state V' to one in which $v_k'=v_k+1$ and $v_l'=v_l-1$ for some pair of normal modes k and l. With this restriction, and assuming harmonic oscillator functions,

$$I_{kl}=\tfrac{1}{2}[(v_k+1)v_l(\nu_l^0/\nu_k^0)]^{\frac{1}{2}}. \quad (9)$$

Finally, there is the third restriction that the coefficient of I_{kl} in G_x, G_y, or G_z must not be too small. This coefficient depends on the nature of the normal modes of vibration k and l so that it is both a geometrical and a dynamical question whether a given pair will have a large coefficient or not.

From this discussion it is evident that before attempting to analyze the rotational fine structure of a given vibration-rotation band of an asymmetrical top molecule by the use of the Wang equation, it is important to investigate the possibility that another vibrational state (which may not give an infrared band) perturbs the upper state of the band in question. If the qualitative tests given above are satisfied, then it may be necessary to use the extended equations given in this paper instead of the Wang equation. This requires either a knowledge of the exact normal modes of vibration or the use of one or more additional empirical parameters (G_x, etc.).

Exactly the same situation may arise in symmetrical top molecules if two nondegenerate states approximately coincide.

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The Crystal Structure of Silver Phosphate

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A new value for the oxygen parameter in the structure of silver phosphate has been determined which gives the P−O separation in the phosphate group as 1.61A±0.03A. The value found here is slightly larger than that determined from an analysis of the crystal KH_2PO_4. The slight increase in P−O distance is explained on the basis of the nature of the phosphate group and of some covalent bond formation between oxygen and the surrounding silver atoms. To get qualitative agreement between calculated and observed intensities it was found necessary to treat the silver atoms as oscillators with tetragonal symmetry, the symmetry of their environments in the crystal. The ratio of the amplitudes of vibration along the tetragonal axis and perpendicular to it has been evaluated from the data. This result is discussed in relation to the structure of silver iodide.

Introduction

A STUDY of the structure of silver phosphate was undertaken to investigate the possible influence of bond formation between the silver and oxygen atoms on the dimensions of the phosphate group. In previous work on this crystal Wyckoff[1] has established it as representing a cubic type structure shown in Fig. 1. The phosphorus and silver atoms are in fixed positions and the oxygen positions on the threefold axes are determined by one parameter. With the methods available at the time Wyckoff was

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[1] R. W. G. Wyckoff, Am. J. Sci. **10**, 107 (1925); Zeits. f. Krist. **62**, 529 (1925).

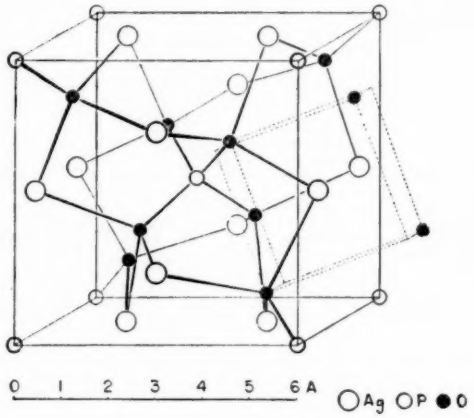

FIG. 1.

able to make a rough estimate of the oxygen parameter, placing it in the neighborhood of 0.25. This value leads to a phosphorus-to-oxygen distance of approximately 2.6A, or nearly 1A larger than the same separation observed by J. West[2] in his careful work on KH_2PO_4. In view of the improved methods now existing for the interpretation of x-ray intensities it has been thought worth while to reinvestigate the structure of Ag_3PO_4 to establish more accurately the distortion of the phosphate group suggested by the earlier work.

In the present work a new value for the oxygen parameter has been obtained which eliminates the large discrepancy mentioned above, and indicates only a slight increase in the P−O distance over the value found for KH_2PO_4. In addition the interpretation of the x-ray data has shown that the silver atoms must be treated as oscillators with tetragonal symmetry the symmetry of the environment of the atoms in the crystal as shown by the dotted lines in Fig. 1. For this case a new temperature factor has been calculated involving, as an additional parameter, the ratio of the force constants along the tetragonal axis and perpendicular to it. In this way it has been possible to account for the data and to obtain a rough idea of the potential function of the silver atoms in the crystal. This result is discussed also in relation to the peculiarities in the intensities of reflection from silver iodide[3] in an attempt to give a more satisfactory explanation of the observed effects.

[2] J. West, Zeits. f. Krist. **74**, 306 (1930).
[3] L. Helmholz, J. Chem. Phys. **3**, 740 (1935).

PROCEDURE

Single crystals of silver phosphate were obtained by redissolving precipitated Ag_3PO_4 in concentrated ammonia solution and allowing the ammonia to escape slowly. This procedure yields small crystals of the yellow solid, the largest obtained being about $1.5\times1.5\times0.5$ mm. The color and habit of these crystals are the same as those given by Groth for Ag_3PO_4 and the unit dimensions checked those given by Wyckoff. These criteria of chemical composition were assumed to be sufficient and the crystals were not analyzed.

Laue and oscillation pictures were taken of three different samples from three different preparations. The Laue photographs were taken by using continuous radiation from a tungsten target with $\lambda_{min}=0.24$A. For the oscillation pictures Mo $K\alpha$ was used. The relative intensities of reflection were obtained by comparing lines of equal intensity on photographs of different exposure times according to the usual practice. A set of five different exposures of 12, 24, 48, 96, and 192 hours, was used to determine the relative intensities given in Table II. The problem of selecting a crystal of the proper size to give reliable intensities is troublesome so that before using the experimental data it was necessary to examine the factors influencing the intensities in order to ascertain how exactly the sample used may be considered to have the properties of (1) a small nonabsorbing crystal, (2) a small absorbing crystal, or (3) a large absorbing crystal which intercepts the entire x-ray beam. For each of these three cases calculation of intensity can be made with some reliability. The intensities given below are taken from photographs obtained with a crystal of dimensions approximately $0.1\times0.1\times0.03$ mm. The assumption has been made that for this crystal absorption and extinction play a negligible role. This assumption is based on the following facts: (1) Lines of the same form reflecting at widely different angles of rotation of the crystal have the same intensity as nearly as can be determined visually. (2) If the explanation of the observed intensity peculiarities is to be found in absorption or extinction effects no solution would result in many cases. This last argument is of a negative nature it is true, but it serves

to give validity to the principal conclusion to be drawn from this work, the tetragonal nature of the temperature motions of the silver atoms. The intensity comparison $I_{(600)} > I_{(601)}$ is an example of this last point and will be discussed later.

The intensity calculations were made by means of the formula

$$I \sim [(1+\cos^2 2\theta)/2 \sin 2\theta]|S|^2 T_f^2$$

where $|S|^2$ is the square of the structure factor and T_f is the temperature factor which will be discussed in detail later. The f values for silver, oxygen and phosphorus were taken from the tables of Pauling and Sherman.[4]

Unit, Space Group, and Approximate Structure

The edge of the cubic unit has been found to be 5.99_5A to be compared with the value obtained by Wyckoff 5.99_3A. The data are given in Table I. Laue exposures of 720 milliampere hours showed no reflections demanding a larger unit. Calculation from the unit size and the density gives the number of molecules in the unit as two. The observed absences (hkl, $h=k$, l odd) permit the space groups O_h^3, T_d^4, O^1, O^2, O_h^1 and T_d^1. The last four may be ruled out by structural and intensity considerations as Wyckoff has shown. O_h^3 may also be eliminated since it does not permit the separate existence of phosphate groups.* The special positions for T_d^4 are:

$2P$ at $000; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.
6Ag at $\frac{1}{2}, \frac{1}{4}, 0; \frac{1}{2}, \frac{3}{4}, 0; 0, \frac{1}{2}, \frac{1}{4}; 0, \frac{1}{2}, \frac{3}{4}; \frac{1}{4}, 0, \frac{1}{2}; \frac{3}{4}, 0, \frac{1}{2}$.
8O at uuu, $\bar{u}\bar{u}u$, $u\bar{u}\bar{u}$, $\bar{u}u\bar{u}$, $\frac{1}{2}+u, \frac{1}{2}+u, \frac{1}{2}+u$; $\frac{1}{2}-u, \frac{1}{2}-u, \frac{1}{2}+u$; $\frac{1}{2}+u$; $\frac{1}{2}-u, \frac{1}{2}-u$; $\frac{1}{2}-u, \frac{1}{2}+u, \frac{1}{2}-u$.

These conclusions are in good agreement with Wyckoff's results.

It will be noticed that the arrangement of the phosphate groups is body centered so that oxygen and phosphorus will not contribute to reflections with $h+k+l$ odd. In addition to the regular space group absences the special positions for the silver atoms lead to the following absences characteristic of this structure type: (hkl) with h, k, and l all odd; (hkl) with $h-k=4n$ ($n=1, 2, 3$ etc.) and l odd.

The absences and intensities can be accounted for in a rough qualitative way on the basis of the structure described above for $u=0.35$. Large discrepancies persist, however, which cannot be due to inaccuracies in the interpretation and which make it necessary to attempt some refinements.

Table I.

(hkl)	sin θ	$d_{(hkl)}$ (exp.)	$d_{(hkl)}$ (calc.)
(200)	0.1189	2.989	2.997
(301)	.1870	1.896	1.896
(400)	.2387	1.498	1.498
(402)	.2640	1.343	1.340
(501)	.3050	1.179	1.176
(502)	.3183	1.114	1.113
(601)	.3680	0.985	0.985
(603)	.3792	0.893	0.894
(702)	.4306	0.823	0.823
(804)	.5285	0.602	0.603

Discrepancies and More Accurate Structure

Long Laue exposures with the x-ray beam making an angle of 7° with the axis [100] show the presence of a reflection from (401) very definitely. As shown above the appearance of this line is not compatible with the special positions of T_d^4 assigned the silver atoms. It does not seem reasonable to attribute the appearance of the reflection to the oxygen atoms for there is no apparent physical reason for moving them from the three-fold axes or placing them in non-equivalent positions. Furthermore lines of the type (401) have been found on Laue and oscillation pictures at angles where the scattering power of oxygen is too small to account for the observed effects.

Another type of disagreement between experimental intensities and those calculated for the above structure is shown by the comparison of the intensities of reflection from (600) and (601). The line (600) is nearly twice as strong as (601) and it reflects at about the same angle of crystal rotation so that absorption cannot be very important. The calculations show that (600) attains its maximum intensity at $u=0.33$, since

* The intensity inequality $I_{(501)} > I_{(431)}$ shows that the oxygen parameter must be larger than 0.30 thus eliminating the possibility of O_h^3. On a symmetrical Laue photograph where these two planes reflect at the same values of sin θ and λ the ratio of intensities is about four whereas for O_h^3 ($u=0.25$) these reflections have the same structure factor.

[4] Linus Pauling and J. Sherman, Zeits. f. Krist. **81**, 1 (1932).

here all the oxygen atoms reflect in phase, and that $I_{(600)} < I_{(601)}$ even at this value of the parameter. It can be seen that neither absorption nor an incorrect oxygen parameter can be responsible for this disagreement.

A number of discrepancies such as this and the appearance of reflections from (401), (801), (621) and a doubtful very faint (841) show that for no value of the oxygen parameter can the calculated intensities even qualitatively be brought into agreement with those observed. It also seems clear that experimental conditions cannot be responsible for these effects.

With the random distribution assigned to silver in some previous work in mind, and believing that there might be some tendency for the silver atoms to form only two bonds to oxygen (as in Ag_2O) I first attempted to get agreement by assigning two possible positions to each silver atom one on each side of the position $\frac{1}{2}, \frac{1}{4}, 0$ along the twofold axis. To do this twelve equivalent positions of T_d^4 were used and a new parameter, p, introduced which gave the separation between the new positions and the original one. The appearance of lines of the type (401) could be accounted for in this way but an attempt to fit the intensities of the other lines failed. In order to force agreement with the experimental data it was found necessary to use eighteen positions, the original six and the twelve new ones and to weight these positions. The best agreement was obtained when the relative weights of the six and twelve positions were 2 : 1, $p=0.035$ and $u=0.34$. In this case it may be added the agreement was only qualitative.

This solution of the difficulty seems unsatisfactory and is, indeed very difficult to interpret physically; it is included here only to show the analogy between this case and that of silver iodide. It was noted that the distribution along the twofold axes corresponding to this solution (with isotropic thermal motion about the points assigned to the fractional silver atoms) it is not greatly different from the probability distribution of an anisotropic oscillator, the various states of which are weighted by an appropriate Boltzmann factor. This suggests that the silver atoms may not behave as spherically symmetrical oscillators but may have a larger amplitude along the twofold axes, i.e., in the directions of the new positions which above have been given the combined weight one-half.

The introduction of this sort of oscillator was accomplished by replacing the temperature factor ordinarily used, of the type $T_f = e^{-\beta(\sin\theta)^2/\lambda^2}$, by a new factor derived on the assumption of an harmonic oscillator with tetragonal symmetry. By using the simple classical method of Darwin[5] the expression for the temperature factor is found to be:

$$T_f = e^{-\beta(\sin\theta)^2/\lambda^2} e^{-\beta(B-1)(\sin\theta)^2/\lambda^2 \cos^2\gamma} = e^{-\beta(\sin\theta)^2/\lambda^2} e^{-\beta(B-1)(h_i/a_0)^2}$$

where β is the exponential coefficient which the factor would have if the force constant along the tetragonal axis were equal to the force constants perpendicular to this direction, B is the ratio of the force constant, perpendicular to the tetragonal axis to that parallel to it and $\cos\gamma$ is the cosine of the angle which the fourfold axis of the oscillators makes with the normal to the reflecting plane. Simple substitution for $\sin\theta$, λ and $\cos^2\gamma$ gives the last expression which is in somewhat more convenient form. Here h_i is the Miller index of the plane along the axis parallel to the tetragonal axis of the oscillator. In the case of this crystal, of course the formula must be applied to each set of two similarly oriented silver atoms in the unit. This is quite simple in practice. A table of $e^{-\beta(B-1)(h_i/a_0)^2}$ against h_i can be set up and the value of $e^{-\beta(B-1)(h_i/a_0)^2}$ can then be quickly multiplied by the f value obtained from the usual f *vs.* $\sin\theta$ curve to obtain the effective scattering factor, since the f value from the curve may easily be computed containing the factor $e^{-\beta(\sin\theta)^2/\lambda^2}$.

The problem is now resolved into one of three parameters, u, β, and B. By means of lines independent of u rough values for β and B were obtained. Lines of this type while showing some qualitative discrepancies for the case $B=1$ are not very sensitive to the actual value of B and more accurate values were obtained by considering all lines by the trial and error method. The evaluation of the parameters was carried out by plotting $I^{\frac{1}{2}}$ against u for a series of values of β and B. In this way the following values were obtained: $\beta=1.75\pm0.25$, $B=2.12\pm0.12$, $u=0.345\pm0.0025$.

[5] C. G. Darwin, Phil. Mag. **27**, 315 (1914).

TABLE II.

PLANE	I(obs.)	I(calc.) $u=0.345$ $B=2.12$ $=1.75$	I(calc.) $u=0.35$ $B=1.00$ $=1.50$	PLANE	I(obs.)	I(calc.) $u=0.345$ $B=2.12$ $=1.75$	I(calc.) $u=0.35$ $B=1.00$ $=1.50$
(200)	7.4	7.8	8.4	(610)	2.45	2.40	2.92
(210)	12.0	12.5	13.5	(611)	1.58	1.53	2.38
(310)	4.6	4.5	4.8	(620)	0.0	0.50	
(320)	7.9	6.9		(630)	2.05	2.04	
(400)	9.1	8.3		(633)	1.0	1.18	
(410)	0.4–0.5	0.56	0.00	(640)	1.32	1.30	
(411)	1.73	1.75	2.42	(641)	1.36	1.44	
(420)	3.45	3.38		(650)	1.32	1.33	
(421)	4.9	4.6		(651)	0.84	0.76	
(431)	0.6	0.6	0.95	(710)	0.0	0.50	
(432)	3.45	3.42		(720)	2.0	2.0	2.00
(440)	6.5	5.3		(721)	1.0	1.15	1.45
(442)	1.32	1.40		(732)	1.23	1.20	1.46
(510)	1.41	1.36	1.40	(742)	1.23	1.25	1.54
(520)	3.75	3.65	3.75	(800)	2.25	2.27	2.70
(521)	2.35	2.30	2.38	(810)	0.47	0.45	0.00
(541)	0.7	0.68		(820)*	0.55	0.54	
(542)	2.26	2.20		(821)*	0.84	0.95	
(550)	0.8	0.72		(840)	1.48	1.41	1.72
(552)	1.22	1.25		(920)	0.90	1.0	
(600)	3.3	3.32	2.65	(921)	0.70	0.65	

* The intensities of these two lines were obtained from long exposure pictures over a small angular range so that the fact that they are calculated weaker than some lines not observed is not significant since these other lines were not in position to reflect on the long exposure pictures.

The data are listed in Table II where the fourth column gives the best calculated intensities for the case of spherically symmetrical oscillation of the silver atoms ($B=1$). The agreement will be seen to be well within the experimental error. In the case of some strong lines, (320), (400), and (404), the error is quite large but here the qualitative relationships are all correct. In the case of some of the weaker lines qualitative disagreements exist, but the difficulties of comparison are here so great that the discrepancies between experimental and calculated intensity are again within the error of the determination. At large angles the lines become somewhat diffuse so that it becomes extremely difficult to make an accurate comparison of integrated intensities. It is true, too, that the total neglect of absorption is not justified. Considered as a whole, however, the agreement between experimental and calculated intensities is probably better than one would anticipate.

The limits of error for β were established by making calculations for $\beta=1.5$ and $\beta=2.0$ and observing that the best fit in these cases was markedly inferior to the agreement obtained with $\beta=1.75$. The limits of error for B were fixed in the same way, calculations being made for $B=2.00$ and $B=2.25$. The lower limit for the oxygen parameter is quite definitely fixed by four reliable comparisons, the upper limit, however, is somewhat more uncertain. At $u=0.3475$ $I_{(200)}=I_{(400)}$; the observed intensity relationship is $I_{(400)}=1.5\times I_{(200)}$. In this case it must be true that absorption has a considerable effect in reducing the relative intensity of (200). The upper limit for u is assigned in the belief that the absorption for this small crystal cannot cut down the intensity by more than one-third.

CONFIGURATION OF THE PHOSPHATE GROUP

The special positions of T_d^4 assigned to oxygen and phosphorus give the configuration of the phosphate group as a regular tetrahedron independent of the oxygen parameter. The parameter value ($u=0.345\pm0.0025$) leads to a phosphorus-to-oxygen distance of 1.61 ± 0.03A, indicating that the P−O separation in this crystal is slightly larger than in KH_2PO_4, in which the potassium-to-oxygen bond is almost certainly ionic. The qualitative considerations given below will show that this effect is reasonable. The phosphorus-to-oxygen distance in the phosphate *ion* is influenced by some double bond formation and some ionic character of the P−O bond itself. Both of these effects presumably tend to decrease the interatomic distance from 1.76A, the sum of the tetrahedral single bond radii according to Pauling and Huggins,[6] to the value 1.56A observed by West. Appreciable covalent bond formation between the oxygen atoms of the phosphate group and the surrounding silver atoms (see Fig. 1) will reduce the number of electrons on the oxygen atoms available for double bond formation and consequently the amount of double bond character of the P−O bonds should decrease. In accordance with the work of Pauling, Brockway and Beach[7] this decrease in the amount of double bond character should show up in an increase in the interatomic distance, and furthermore, in a case such as that under consideration where here the bond has

[6] L. Pauling and M. L. Huggins, Zeits. f. Krist. **87**, 205 (1934).

[7] Pauling, Brockway and Beach, J. Am. Chem. Soc. 57, 2705 (1935).

fifty percent or more double bond character, the above work shows that a slight change in the amount of double bond character will have only a very small effect on the interatomic distance. One may deduce that the change in double bond character will be small from the fact that it depends on the covalent character of the Ag−O link which seems to be very nearly ionic since the interatomic distance here found is 2.34A±0.01A, or very nearly the sum of the ionic radii when corrected for coordination number. The sum of the covalent radii is by contrast 2.18A.

It is difficult to estimate the influence of the ionic nature of the P−O bond. The formation of a Ag−O covalent bond should increase the ionic character of the P−O bond while at the same time the decrease in double bond formation should diminish it. On the basis of the experimental data one must conclude that the effect of diminished double bond formation outweighs that of increased ionic character, and, as a consequence of this, that the normal structure of the phosphate ion is essentially covalent.

The Temperature Vibrations of the Silver Atoms

The value obtained for B, the ratio of the force constants perpendicular and parallel to the fourfold axes of the silver oscillators gives an amplitude of vibration along the tetragonal axis 1.46 times as large as the amplitude perpendicular to this direction, if one makes use of the assumptions involved in the calculation of the temperature factor, a harmonic oscillator for which the amplitude is inversely proportional to the square root of the force constant. To check this result a simple calculation has been made in which the silver-oxygen bonds have been treated as springs with no resistance to bending. With the dimensions taken from the crystal this calculation leads to a value of B equal to 2.75, or a ratio of the amplitudes of vibration equal to 1.65. The agreement here is probably well within the combined errors of calculation and experiment. The calculation of the temperature factor is unquestionably oversimplified. Certainly a consideration of the restoring force for bending of the bonds (if there is appreciable covalent character) would lead to closer agreement.

Discussion of Silver Iodide and Bromide

In a previous paper[3] it has been shown that the x-ray spectra of AgI at temperatures from 100°C to −180°C may be accounted for by assuming a random distribution of silver atoms among five positions inside the tetrahedron formed by the surrounding iodine atoms; one position in the center and four displaced toward the four faces of the tetrahedron. This structure for silver iodide may be changed in accordance with the procedure used in the case of silver phosphate. Here, however, the use of Hooke's law forces leads to spherical symmetry for the atomic vibrations, and the anomalies of the x-ray spectra cannot be explained so simply. It is necessary to introduce fourth power terms into the potential function, and the calculation of the corresponding temperature factor becomes quite complicated. If we assume fourth power terms giving the potential functions for the silver and iodine atoms tetrahedral symmetry we may argue by analogy with the silver phosphate crystal that these potential functions must have a smaller slope in the directions of the faces of the surrounding tetrahedra since it was in these four directions that fractional parts of silver atoms were moved to get agreement with experiment. We are now permitted to treat iodine and silver atoms alike which seems more satisfactory than the assumption of special positions for silver alone (it is true, however, that we cannot expect the two atoms to show the same degree of anharmonicity). If the silver and iodine tetrahedra were similarly oriented, one would expect no marked effect other than a decrease in scattering power, but in the wurtzite structure they are oppositely directed along the c-axis. This means that the anharmonic character of the vibrations of each atom contributes to the anomalies observed and that the differences in the amplitudes of vibration need not be very great to account for the observed effects.

Photographs taken of AgI at low temperatures (−180°C) indicated that the structure was essentially that of wurtzite with the ideal value of the parameter. Two reflections, (10·9) and (00·12) were in disagreement with this conclusion, (00·12) by a factor of ten. The assumption was made in the previous paper that of the five potential minima in each silver tetrahedron

the central one had the lowest energy so that with decreasing temperature the atoms would tend to settle in this position, but that at the temperature of the experiment only about four-fifths of them had done so. The explanation of the temperature effects becomes much simpler on the basis of the structure proposed here, and one would expect the discrepancies to persist even to 0°K because of the existence of zero-point vibrations, though they would naturally be small.

The structure to be assigned to silver iodide on the basis of these considerations is that of ideal wurtzite in which the silver and iodine atoms behave as anharmonic oscillators having larger amplitudes in the directions of the faces of the tetrahedra formed by the nearest neighbors than in the directions of the corners of the tetrahedra. The fact that the effect is observed for this crystal and not for others with the same type structure is due probably to the fact that in this case of a very soft crystal the temperature factor and so the amplitudes of vibration are so large that the effects outlined above can be detected by the use of relative intensities obtained photographically.

An attempt has been made to find a similar effect for AgBr. That such an effect should exist seemed reasonable from the previous explanation of the structure of the iodide. No discrepancies between the observed intensities and those calculated for the ideal sodium chloride structure have been found. The temperature factor, $\beta=3.5$ is rather high but what one would expect for such a soft crystal. If, as in the two previous cases we are to believe that observed discrepancies are to be attributed to deviations of the temperature motions from spherical symmetry, we can see quite easily that in the case of AgBr none should arise, for, not only would it be difficult to distinguish an oscillator with octahedral symmetry, the symmetry of the environment of Ag and Br atoms (or ions), from one of spherical symmetry, but in this case also the octahedra have the same orientation with respect to the reflecting planes so that no large effect would be observed in any case. If this analysis is correct one must attribute the deviations from additivity of ionic radii in the interatomic distances of the silver halides, which are intermediate between the sums of the covalent and ionic radii to an intermediate character of the bonds or, to what is equivalent, to polarization.

The phenomenon outlined above should be found wherever the environment of an atom is greatly different from spherically symmetrical. A clear cut observation of the effect in x-ray investigations will be dependent upon the orientation of the potential functions of the atoms with respect to the reflecting planes. This should be clear from the discussion of the cases of silver iodide and bromide. The effect will also vary in degree dependent on the magnitude of the force constants since it depends to a large extent on β as will be seen by reference to the temperature factor developed for the case of silver phosphate. The anisotropic character of atomic vibrations should show up strikingly in soft crystals containing atoms with square coordination, or atoms which form two opposed bonds. PdO and K_2PtCl_4 are examples of the first class. For the first compound the data are insufficient for accurate analysis but in the second case some discrepancies between calculated and observed intensities in Dickinson's work on K_2PtCl_4[8] can be explained on the basis of tetragonal symmetry for the oscillations of the platinum atoms. The cuprite type structure is an example of the second class but here it is easy to see that the orientation of the O−Cu−O bonds makes it probable that the detection of the anisotropy of motion would be difficult to detect without accurate intensity measurements. It is probably true, too, that in many crystals where the configurations would allow the observance of the effects outlined the temperature oscillations are of such small amplitude at toom temperature that the departure from spherical symmetry would not have a great influence on the x-ray spectra.

I am indebted to Professor Linus Pauling for discussion of this work and helpful suggestions.

Note added in proof: Since the writing of this paper two articles treating the subject of anisotropic thermal motions of crystals have come to my attention, a theoretical discussion of the phenomenon by Zener in the *Physical Review* of January and a note on the observation of the effects for the cases of Cd and Zn by G. W. Brindley in the February issue of *Nature*.

[8] R. G. Dickinson J. Am. Chem. Soc. **44**, 2404 (1922).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the latter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Conductance of Salt Crystals

Recently Rodebush and Cooke[1] criticized a paper of the author[2] in a way which hardly seems adequate.

(1) It is commonly known, as assumed in my article, that generally the conductance cannot be represented over the whole range of temperature by a single exponential. It was the aim of my investigation to show that for regions, where a simple exponential holds—this is always the case for unipolar conductors and sufficiently high temperatures—one can derive the *correct formula with constants of the right order of magnitude*. Then it is not difficult to generalize the result for more complicated cases. Of course one can derive the same formal expression by more or less vague analogies with reaction rates as has been shown sufficiently often since the time of Rasch and Hinrichsen.[3]

(2) Rodebush and Cooke's attempt of a derivation of the self-diffusion formula is not without contradiction within itself. It holds generally that properties belonging to a *stationary* state—and self-diffusion as well as electrolytic conduction refer to a stationary state—cannot be derived by analogies with the rate of a reaction without an explicit consideration of the reverse reaction. Rodebush and Cooke's reasoning contains instead of the reverse reaction only the loss of mobility of an activated ion which moved away from its former lattice point. *Therefore they describe the crystal in a state of increasing perturbation ("Fehlordnung"), not considering where the dislocated ions shall remain.* A consequent treatment, however, would require as reverse reaction the return of an activated ion into a normal lattice position; therefore one first has to assume that vacant lattice points are present. If Rodebush and Cooke had consequently carried through their reasoning they would have arrived at the conclusion that in equilibrium a certain fraction of the ions must be dislocated to irregular positions, leaving empty lattice points at their former positions; but this is just the model used by Frenkel[4] and the author. In special cases such empty positions are present in the original lattice structure as in the cases of $\alpha-AgJ$[5] and $\alpha-Ag_2S$[6] which have been found after the author's first paper.

(3) Usually the methods of statistical mechanics and thermodynamics give more precise results in the treatment of states of equilibrium than in kinetic problems. Especially for the treatment of disturbances of a crystal lattice ("Fehlordnungs-Erscheinungen") the existence of which can be concluded from numerous observations we refer to the fundamental papers of Schottky and Wagner.[7] We mention, however, that the author's assumption of the existence of an *equivalent* number of "holes" and dislocated ions is not always true; for instance it may happen that the number of dislocated ions is negligible compared with the number of "holes" of both signs, which probably holds in the case of alkali halides.[8,9]

W. Jost

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Hannover, Germany,
March 25, 1936.

[1] W. H. Rodebush and T. G. Cooke, J. Chem. Phys. **3**, 834 (1935).
[2] W. Jost, J. Chem. Phys. **1**, 466 (1933).
[3] E. Rasch and F. W. Hinrichsen, Zeits. f. Elektrochemie **14**, 41 (1908).
[4] I. Frenkel, Zeits. f. Physik **35**, 652 (1926).
[5] L. W. Strock, Zeits. f. physik. Chemie **B25**, 441 (1934).
[6] P. Rahlfs, Zeits. f. physik. Chemie **B31**, 157 (1936).
[7] C. Wagner and W. Schottky, Zeits. f. physik. Chemie **B11**, 163 (1930); C. Wagner, Zeits. f. physik. Chemie, Bodenstein Festschrift, (1931), p. 177; Zeits. f. physik. Chemie **B22**, 181 (1933); C. Wagner, Physik. Zeits. **36**, 721 (1935).
[8] W. Schottky, Zeits. f. physik. Chemie **B29**, 335 (1935).
[9] cf. W. Jost, Zeits. f. tech. Physik **16**, 363 (1935).

The Raman Spectrum of Oxalic Acid

In a recent note Angus and Leckie[1] have taken exception to an observation of Hibben made in a previous publication.[2] This article recorded and discussed the Raman spectrum of oxalic acid in aqueous and alcoholic solutions, as the dihydrate and as the anhydrous compound. It was observed, in comparison with other organic acids, that the two C=O Raman shifts ($\Delta\tilde{\nu}$ 1645 and 1740) obtained from anhydrous acid and aqueous solution are anomalous. In alcoholic solutions the doubling of the carbonyl shift no longer occurred and one shift, $\Delta\tilde{\nu}$ 1755, resulted, which is more in accord with the carbonyl shift obtained from an ester, aldehyde or ketone. Consequently it was affirmed that, based on the magnitude of the two frequency displacements, the two carboxyl groups behave differently in aqueous solution and in the anhydrous acid, but identically in alcohol. The attribution of $\Delta\tilde{\nu}$ 1430 to an O−H shift in oxalic acid by Rao,[3] Tschitschibabin's and the hexahydroxy formulas were discussed in detail.

In addition to the above, which comprised the greater portion of the article in question, it was stated: "No shifts corresponding to those at approximately $\Delta\tilde{\nu}$ 1650 and 1750 of the anhydrous acid were observed in the hydrate. This

does not preclude the possibility that they may be extant, but if so they are very much weaker than the same shifts in the dehydrated acid." It is principally with this remark that Angus and Leckie disagree, as they state: ". . . the Raman spectra obtained from the saturated aqueous solutions of oxalic acid and from the dihydrated oxalic acid crystals are substantially the same." However, they add: "Our results, obtained from crystals which were definitely dihydrate crystals, agree with those of Rao . . ." and, "Since Hibben's conclusions that the two carboxyl groups behave differently depend to a large extent on the difference in the spectra of the anhydrous and hydrated crystals we submit that such conclusions may be invalidated by his comparing the spectrum he obtained for his anhydrous crystals with Rao's spectrum for the solid."

The last quotation leaves such an erroneous impression that it is necessary to correct it. As pointed out in the first paragraph of this note, the different behavior of the two carboxyl groups is predicated on the observed magnitudes of the two carbonyl shifts and not on a comparison of the anhydrous, or hydrated material with the solution, consequently these conclusions are not affected by the presence or absence of such shifts in the hydrated material.

The apparent weakening of these lines in the anhydrous acid and their greater weakening (or absence) in the hydrated compound were explained by this writer as possibly attributable to chelation. If Angus and Leckie's observations are correct this explanation would be without significance. Nevertheless Rao's results cannot be cited in entire support of themselves since his published photographs show clearly that in the hydrate or anhydrous acid (it is immaterial to the argument which he used) the relative intensities of the carbonyl frequencies are markedly reduced as compared with the solution, in contradistinction to the first statement of Angus and Leckie's previously quoted. The intensities published by Rao are: (for $\Delta\tilde{\nu}$ 1640 and 1740, respectively) crystal: 00, 1; solution: 1, 3; or approximately a 66 percent decrease taking $\Delta\tilde{\nu}$ 845 as a reference standard. It is unfortunate that in republishing Rao's data Angus and Leckie omitted the intensities, which indicate an agreement with the present writer.

The fact that carbonyl shifts may weaken is already well known from the spectra of acid salts. So far as the hydrate is concerned Zachariasen[4] from x-ray measurements has concluded that the C−O bond in this compound is at least part of the time a single bond, and that this substance is not a normal hydrate of oxalic acid.

It is believed that some of the difficulties of interpretation may have arisen in the use of an unfiltered mercury spectrum as a source of excitation. The O−H band, unusually sharp, falls in approximately the same position as the C=O shifts and the 4730 Hg line overlaps in the same position.

JAMES H. HIBBEN

Geophysical Laboratory,
Carnegie Institution of Washington,
January 21, 1936.

[1] Angus and Leckie, J. Chem. Phys. **4**, 83 (1936).
[2] Hibben, J. Chem. Phys. **3**, 675 (1935).
[3] S. Rao, Zeits. f. Physik **94**, 536 (1935).
[4] Zachariasen, Phys. Rev. **45**, 755 (1934).

Reply to Dr. Hibben's Letter

Dr. Hibben's criticisms may be answered very briefly. His suggestion that our results for the dihydrate crystals are vitiated by incomplete filtration of the 4047A Hg line is incorrect since we used a strong solution of $NaNO_2$ as a filter and the 4047 undisplaced Hg lines were very weak on the plates. His second quotation from our letter tends to misrepresent the arguments put forward by us. We must maintain our view that Rao's crystals, showing frequencies at approximately 1660 and 1760 cm^{-1}, were dihydrate crystals and that Rao's results, therefore, support our own observations. We have satisfied ourselves that our results are correct.

The purpose of our letter was merely to indicate differences in results which, as we pointed out, *may* invalidate some of Hibben's conclusions. We do not think that the point at issue is sufficiently important to merit an extended controversy.

W. ROGIE ANGUS
ALAN H. LECKIE

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London, W.C.1.,
February 19, 1936.

Metallic Binding According to the Combined Approximation Procedure

A combined approximation procedure has been proposed by one of us[1] for the calculation of the chemical interaction between atoms. In this method the atomic kernel is treated according to Thomas-Fermi and the valence electron by a Schrödinger equation. The total action of the kernel upon the valence electron—inclusive of the Pauli principle—then goes over into an additional potential in the Schrödinger equation, which can be taken approximately from the spectra. The application to K_2 and KH gave plausible results, however, on account of the omission of higher approximations they were still not absolutely convincing. We have therefore applied the combined approximation procedure to the problem of metallic binding. Here one can easily take into account the interactions between the valence electrons to a higher degree of approximation than in single molecules.

It was established in the beginning that the law $-1/r+(A/r)e^{-2\kappa r}$ for the total field of the kernel gives a good approximation in the case of the free Mg atom: When A and κ were so determined that the lowest s term and p term of Mg^+ were rendered correctly, then Ritz's method (with r_{12} in the eigenfunction) yielded good results for the ground term of Mg. For the alkali metals A and κ were determined from the two lowest s terms with the aid of one-parameter hydrogen-like eigenfunctions. Since the field of the ion determined in this way runs a rather flat course, it is sufficient in the first approximation to set the valence electron in the lattice equal to a plane wave. The interaction of the kernels arising from their overlapping is

neglected. The energy of the metallic lattice is then composed of the following parts:

(1) Electrostatic energy $\sim -1/d$ (taken from Wigner and Seitz[2])
(2) Exchange energy after Bloch[3] $\sim -1/d$
(3) Correlation energy after Wigner[4] (from Fig. 7 of [4])
(4) Thomas-Fermi energy $\sim 1/d^2$
(5) Additional energy = El. density $\times \int \frac{1}{r} e^{-2\kappa r} d\tau = \frac{2\pi A}{\kappa^2} \frac{1}{d^3}$.

The Table I gives the values found in this way for the heat of sublimation and d_0*. Through improvement of the uniform distribution of the valence electron in the lattice, a further approach of the heat of sublimation to the experimental value may be attained. That the additional energy reproduces well the influence of the kernels upon the valence electron is demonstrated by the calculated $\partial^2 E/\partial V^2$ which agrees much better with the experimental data than the calculation of Rice,[5] who instead of our introduction of the additional energy assumed the kernels to be impenetrable and determined their radius empirically from d_0 itself. The relationship between sublimation energy, ionization energy and the work function first established by Wigner and Bardeen[6] is also valid in this theory.

TABLE I.

	Lattice Const. (A)		Binding Energy (ev)		$\partial^2 E/\partial V^2$ (E: Energy, V: Atomic Volume) (10^{23} erg·cm^{-6})			Work Function (ev)	
N/a	calc.	exp.	calc.	exp.[5]	calc.	exp.[5]	calc. Rice[5]	calc.	exp.[6]
Na	4.35	4.24	0.91	1.13	1.59	1.9	4.7	1.96	2.25–2.46
K	5.20	5.25	0.85	0.94	0.47	0.53	1.33	1.95	2.17–2.24
Rb	5.75	5.62	0.594	0.865	0.24	0.17	0.89	1.90	2.16–2.19
Cs	6.15	6.05	0.599	0.83	0.15	0.065	0.58	1.86	1.81–1.96

Column 4 gives the work function calculated in this way, omitting the double layer term. When one bears in mind that the only empirical data used are the spectra of the free atoms the agreement is satisfactory and there is the hope that this simple approximation method will prove useful for further metallic problems where the more vigorous methods become involved in formal difficulties.

The complete work will appear in the *Acta Physicochimica U.R.S.S.*

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W. KASSATOTSCHKIN

Karpow-Institute for Physical Chemistry,
Moscow,
March 15, 1936.

* Li was omitted, as in this case the application of a statistical method is not free of arbitrariness.

[1] H. Hellmann, J. Chem. Phys. **3**, 61 (1935); Acta Physicochimica U.R.S.S. **1**, 913 (1935); **4**, 225 (1936).
[2] E. Wigner and F. Seitz, Phys. Rev. **46**, 509 (1934).
[3] F. Bloch, Zeits. f. Physik **57**, 545 (1929).
[4] E. Wigner, Phys. Rev. **46**, 1002 (1934).
[5] O. K. Rice, J. Chem. Phys. **1**, 649 (1933).
[6] E. Wigner and J. Bardeen, Phys. Rev. **48**, 84 (1935).

The Raman Spectra of Carbon and Silicon Tetrafluorides

We have photographed the Raman spectra for the tetrafluorides of carbon and silicon in both the liquid and gaseous states. The results are presented in Table I together with the Raman frequencies of CCl_4 for purposes of comparison. The relative intensities are given in parentheses.

TABLE I.

	ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})	ω_4 (cm^{-1})
CF_4	904 (10)	437 (1)	(1200)	635 (1)
SiF_4	800	(285)	(1000)	(431)
CCl_4	450	214	775	311

So far only ω_1 for SiF_4 has been found, the other three lines being apparently of small intensity. For gaseous CF_4 only ω_1 was definitely seen on the plates, and it was sharp and strong. ω_2 and ω_4 together with ω_1 were obtained from CF_4 (1) at $-120°$.

The CF_4 was prepared by treating carbon (Norit) with fluorine gas and submitting the raw product to a number of fractional distillations. It is difficult to prepare pure CF_4. The SiF_4 was prepared by a conventional method.

The assignment of frequencies is based on a number of considerations. Since ω_1 is the completely symmetrical vibration, it should appear intense and sharp in the Raman spectrum. Accordingly the strongest and sharpest observed line was assigned to ω_1. It was found, from a consideration of the Raman spectra for eight tetrahalides that certain regularities existed (approximate constancy of ratios of corresponding frequencies), and on the assumption that no discontinuities in these regularities would occur with CF_4 the frequencies ω_2 and ω_4 were assigned.

The frequencies given in parentheses were computed from empirically found ratios, or from the formulae derived from normal coordinate treatments of tetrahedral molecules by Urey and Bradley,[1] and Rosenthal.[2]

Two absorption bands in the infrared spectrum of CF_4 have been observed recently by Eucken and Bertram,[3] namely, $\omega_3 = 1350$ cm^{-1} and $\omega_4 = 653$ cm^{-1}. The latter is in fair agreement with 635 cm^{-1} found in the Raman spectrum, and the estimate (1200) for ω_3 is, considering the theory involved, in accord with $\omega_3 = 1350$ cm^{-1}. Eucken and Bertram estimate ω_2 to be 503 cm^{-1} from specific heat measurements, and this agrees only moderately well with the observed value, $\omega_2 = 437$ cm^{-1}. The disagreement is probably to be assigned to errors in the theory or measurement of the specific heats.

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California Institute of Technology,
Pasadena, California,
April 6, 1936.

[1] Urey and Bradley, Phys. Rev. **38**, 1970 (1932).
[2] Rosenthal, Phys. Rev. **45**, 538 (1931).
[3] Eucken and Bertram, Zeits. f. physik. Chemie **B31**, 361 (1936).